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ABSTRACTS OF PAPERS
ON
ORGANIC CHEMISTRY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Electro-syntheses. IV. SIMA M. LOSANITSCH (*Ber.*, 1909, **42**, 4394—4400. Compare Abstr., 1908, i, 2, 846, 866; ii, 32).—The substances investigated were submitted to the action of the silent electric discharge.

*iso*Pentane absorbs oxygen from the air, and is condensed to a mixture of higher saturated and unsaturated products, in which the latter predominate. *n*-Hexane is more slowly acted on; in this case the saturated products predominate.

Ethyl ether breaks down into formaldehyde, methane, and ethylene. The condensation products C_4H_8O and $C_8H_{14}O_2$ are formed, also ethylal, derived from formaldehyde and ether.

Acetaldehyde is decomposed to the extent of 80%, and condensed to 20% only. The decomposition products are mainly carbon monoxide and methane. The condensation products are polymerides of acetaldehyde and formaldehyde with aldehydic characteristics.

Formic and acetic acids are decomposed. Ethyl acetate gives hydrogen, methane, and carbon monoxide. The condensation products are $C_4H_8O_2$, corresponding with a bimolecular acetaldehyde, $C_5H_{10}O_3$, a combination of formaldehyde and ethyl acetate, and $(C_4H_8O_2)n$, a higher polymeride of acetaldehyde. Chloroform yields an oil, $C_6H_2Cl_{12}$, and hexachloroethane.

Ethylene yields a volatile product, $C_{16}H_{30}O$, and a non-volatile product, $C_{26}H_{44}O_2$.

Benzene gives a volatile product, $(C_6H_6)_n$, and a non-volatile compound, $C_{24}H_{26}$.

Benzene and hydrogen form a colourless, oily, volatile liquid, $C_{12}H_{14}$, and a non-volatile, red, thick, clear substance, $C_{28}H_{34}$. E. F. A.

Formation of Naphthenes in Mineral Oil. I. CARL ENGLER (*Ber.*, 1909, **42**, 4610—4613).—It is shown conclusively by the author, in conjunction with Routala (compare following abstracts), that olefines, which are formed by the distillation of fats under pressure, when heated under pressure at about 200° readily yield naphthenes and substances closely resembling mineral lubricating oils; consequently, the assumption that the naphthenes in mineral oils owe their origin to the action of a catalyst on olefines is unnecessary (compare Aschan, Abstr., 1902, i, 749). W. H. G.

Formation of Naphthenes. II. Action of Aluminium Chloride on Amylene at Low and Moderately High Temperatures. CARL ENGLER and O. ROUTALA (*Ber.*, 1909, **42**, 4613—4620).—A detailed account of the behaviour of various samples of amylene when treated with aluminium chloride at the ordinary temperature and at about 130°. Generally speaking, the results obtained are in good agreement with those recorded by Aschan (Abstr., 1902, i, 749); thus, the more volatile products are composed mainly of paraffins, such as pentane, *iso*pentane, hexane, $\beta\gamma$-dimethylbutane, γ-methylpentane, heptane, octane, decane, etc., whilst traces of naphthenes are present only in the fractions with high boiling points. W. H. G.

Naphthene Formation. III. Products Formed by Heating Amylene and Hexylene Under Pressure. CARL ENGLER and O. ROUTALA (*Ber.*, 1909, **42**, 4620—4631).—When commercial amylene (β-methyl-Δ^{β}-butylene) is heated under pressure at 320—325° for thirty-two days, it yields a gas (about 10 litres from 350 grams) and a liquid with a bluish-green fluorescence. The gas is composed of saturated hydrocarbons, paraffins, and polymethylenes, 91·1%; unsaturated hydrocarbons, 1·5%, and hydrogen, 7·4%. The liquid when fractionally distilled yields various paraffins, such as pentane, *iso*pentane, hexane, heptane, and octane, whilst the higher boiling fractions (b. p. 130—250°) consist almost solely of naphthenes identical with, or very similar to, those which have been isolated by Markownikoff and Oglobin from Caucasian petroleum; for example, fractions were obtained having the composition and physical properties of nononaphthene, *iso*decanaphthene, β-decanaphthene, hendecanaphthene, tetradecanaphthene, and pentadecanaphthene; in addition, α-decanaphthene was isolated and identified as the nitro-derivative. The fractions with high b. p.'s closely resemble the mineral lubricating oils.

Δ^{β}-Hexylene (methylpropylethylene), when heated under pressure at 325° for about thirty days, yields a mixture of gaseous, saturated hydrocarbons, and an oil from which fractions were obtained similar to those derived from amylene. W. H. G.

Chloroethylenes. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, **42**, 4481—4485).—Whilst ethylene, its homologues and analogues combine rapidly with mercury salts, especially in presence of sodium acetate, di-, tri-, and tetra-chloroethylenes undergo no change under these conditions. With alkaline mercuric cyanide solutions, these haloid derivatives form salt-like, substituted compounds, the ethylene linking remaining intact (compare Abstr., 1908, i, 145); further, they are gradually reduced by platinum chloride, with which ethylene itself combines.

Iodine does not yield additive products with di-, tri-, or tetra-chloroethylene in the dark; with the trichloro-compound a slow action occurs in daylight, but the change is more complicated than simple addition.

The addition of bromine to these haloid derivatives in carbon tetrachloride solution in the dark takes place with measurable velocity (compare Plotnikoff, Abstr., 1906, ii, 12; Herz and Mylius, Abstr., 1907, i, 55; Bauer and Moser, Abstr., 1907, i, 307). With dichloroethylene the value of K calculated for a reaction of the second order is constant ($1{\cdot}18$—$1{\cdot}52.10^{-4}$). With tetrachloroethylene the value of K increases to an approximately constant magnitude, the auto-acceleration of the reaction being due to the catalytic action of an oxidation product, such as carbonyl chloride, the odour of which is observable.

In the case of trichloroethylene the reaction is very complex and irregular. The velocity, which initially is greater than with dichloroethylene, diminishes from $K = 4{\cdot}06 \times 10^{-4}$ to $0{\cdot}58 \times 10^{-4}$, afterwards increasing to the value $2{\cdot}57 \times 10^{-4}$. Here, also, the odour of carbonyl chloride is noticed, and either this compound or an analogous oxidation product doubtless exerts a considerable catalytic influence on the reaction. T. H. P.

Esters of Perchloric Acid. KARL A. HOFMANN, [GRAF] ARMIN ZEDTWITZ, and H. WAGNER (*Ber.*, 1909, **42**, 4390—4394. Compare Abstr., 1909, ii, 568).—The attempt was made to prepare alkyl esters of perchloric acid by the interaction of nitrosyl perchlorate with alcohols. These perchlorates are formed, but even when very small quantities of substance are used and every precaution is adopted, they are of too explosive a nature to be isolated. The experiments were accordingly restricted to the preparation of esters of ethylene glycol and chlorohydrin, formed by the interaction of ethylene oxide and of epichlorohydrin with perchloric acid, D 1·72, containing sixty-three parts by weight of $HClO_4$.

Chloroperchloratohydrin, $ClO_4{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$, is a colourless, heavy oil. It burns like gun-cotton, explodes when struck more easily than nitroglycerin, but is easily hydrolysed by water and slowly decomposes in moist air. This excludes any practical application as an explosive.

The corresponding *chloronitratohydrin* does not explode, and is hardly hydrolysed at $+17°$ under conditions which cause hydrolysis of more than half of the perchlorate.

Diethylene glycol monoperchlorate, $ClO_4{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_4{\cdot}OH$, is a colour-

less oil, which explodes violently when heated and burns like gun-cotton. It is slightly more stable towards moisture than the chloroperchloratohydrin, but slowly decomposes when exposed to the atmosphere.

E. F. A.

Sodium Alkyl Carbonates. ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 303—304).—Sodium methyl and ethyl carbonates have been obtained by the action of dry carbon dioxide on the dry sodium alkyl oxide free from alcohol. Both substances are decomposed by water, but not by acetone, or yet when heated to about 180°. Whilst sodium phenyl carbonate is decomposed by acetone, it is shown that the rate of decomposition is greatly reduced if the acetone is dried over phosphoric oxide. H. M. D.

Kephalin. JAKOB PARNASS (*Biochem. Zeitsch.*, 1909, **22**, 411—432).—Kephalin was prepared by extracting the hardened and dried brain with light petroleum. It was separated from the cholesterol and phosphatides by precipitation from this solution by alcohol. From the precipitate thus obtained it was extracted by a small quantity of very cold ether, and thus separated from the cerebrosides. The ratio of P : N in the carefully prepared product is 1 : 1. It readily undergoes hydrolysis with water, acids, and bases. On heating at 120° for twelve hours with barium hydroxide solution, it yields stearic acid, bases, and a barium salt, $C_{27}H_{53}O_{10}PBa_2$, the acid of which is obtained in a yield of about 50% of the kephalin hydrolysed.

On further hydrolysis with alkali, this phosphorus-containing tetrabasic acid yields "kephalinic" or "kephalinolic" acid in a yield equivalent to 18% of the kephalin. This was obtained pure in the form of the *methyl* ester, $C_{19}H_{34}O_2$, which, on treatment with hydrogen, is converted into methyl stearate, m. p. 37°, from which stearic acid, m. p. 69°, was obtained on hydrolysis. The kephalinic acid ester also takes up 1 molecule of oxygen on treatment with air. The free acid obtained from the ester by hydrolysis solidifies on cooling to −8°, but melts on warming to −4°. It boils at 205° in a vacuum, yielding apparently a mixture of free acid and the isomeric lactone. The barium salt, $(C_{18}H_{31}O_2)_2Ba$, is crystalline. The acid can be directly reduced by hydrogen in the presence of palladium to stearic acid. The sodium salt is soluble in ether. The author brings forward reasons for believing that kephalin is constituted differently from the lecithins. S. B. S.

α-Bromopropionic Acid. LUDWIG RAMBERG (*Annalen*, 1909, **370**, 234—239).—I. *l-α-Bromopropionic Acid.*—This acid has been carefully purified by repeated crystallisation and separation of the crystals from the liquid acid by means of a centrifuge; it has m. p. −0·3° to −0·5° (in a sealed capillary tube), D_4^{20} 1·700, D_4^{25} 1·692, $[\alpha]_D^{20}$ −29·0°, $[\alpha]_D^{25}$ −28·5° (compare Abstr., 1906, i, 923). The acid racemises very slowly, the value of $[\alpha]_D^{20}$ changing from −27·0° in May, 1906, to −24·3° in July, 1909.

II. *Inactive α-Bromopropionic Acid.*—A metastable modification of this acid has been obtained by rapidly cooling the liquid acid to $-30°$; it has m. p. $-3\cdot9°$ (corr.), and is very stable in the absence of the stable variety, but by inoculation changes spontaneously into this acid. The stable form has m. p. 25·7° (corr.), D_4^{20} 1·700 (compare Weinig, Abstr., 1895, i, 16), and is undoubtedly the true racemic form of the acid. W. H. G.

Melting and Solidifying Points of Fatty Substances. I. Binary Mixtures of Stearic, Palmitic, and Oleic Acids. EMILIO CARLINFANTI and MARIO LEVI-MALVANO (*Gazzetta*, 1909, **39**, ii, 353—375).—The authors discuss the various methods which have been suggested for the determination of the m. p. of fats, and give the results of their investigations on the solidification curves for the systems palmitic-stearic, palmitic-oleic, and stearic-oleic acids.

The solidification diagram for palmitic-stearic acid consists of two curves, the one for the system having for components stearic acid and the additive compound, $C_{16}H_{32}O_2,C_{18}H_{36}O_2$, and the other for the system comprising the additive compound and palmitic acid. The first of these curves, which meets the other at 56°, the crystallisation temperature of the additive compound, is of Roozeboom's type I, and shows neither a maximum nor a minimum, the solidifying point of stearic acid being lowered continuously by addition of the additive compound. The second curve is a combination of Roozeboom's types II and III, and exhibits a maximum at 56·25° and a minimum at 54·75°, neither of these temperatures corresponding with a simple compound of the two components. The additive compound hence forms with palmitic acid three different series of solid solutions.

The diagram for mixtures of stearic and oleic acids is of Roozeboom's type I, the m. p. of stearic acid being depressed at first slowly and afterwards rapidly as the addition of oleic acid is continued. These acids hence form a continuous series of solid solutions (compare Garelli and Montanari, Abstr., 1895, ii, 205). The mixture containing 5% of stearic acid begins to crystallise at 12·4°, after a superfusion of 0·2°, the temperature falling gradually to 7·8°, where a sudden jump to the solidification point of oleic acid takes place, followed by a very slow fall of temperature. This behaviour is explained by the separation at 12·4° of a solid solution, which is richer in stearic acid than the liquid, and does not enter into equilibrium with the liquid, that is, does not absorb oleic acid as the temperature falls. Gottlieb (*Annalen*, 1846, **57**, 37) gave for oleic acid the m. p. 14° and the solidifying point 4°; for their oleic acid, which gave an iodine number of 90·5 instead of the theoretical 90, the authors found the solidifying point 9° with 2·5° superfusion.

The system comprising palmitic and oleic acids exhibits behaviour similar to that of stearic and oleic acids.

The additive compound formed by palmitic and stearic acids probably represents the original margaric acid, the more recent daturic acid, and, possibly, the synthetic margaric acid assumed to exist at the present day. T. H. P.

Melting and Solidifying Points of Fatty Substances. II. Ternary Mixtures of Palmitic, Stearic, and Oleic Acids. EMILIO CARLINFANTI and MARIO LEVI-MALVANO (*Gazzetta*, 1909, **39**, ii, 375—385. Compare preceding abstract).—In order to obtain data for the determination of the proportions of palmitic, stearic, and oleic acids in a mixture of the three, the authors have investigated the solidifying points of fifty mixtures of the three acids.

With each mixture, the temperature falls regularly while the mixture remains liquid, rises 1—1·5° when crystallisation commences, then again falls slowly until crystallisation is complete, and subsequently more rapidly. In no case is an arrest of the temperature observed during the fall, so that the solid formed by the crystallisation of any one mixture of the acids is formed of a single phase, composed of solid solutions of the three acids, the miscibility of these in the solid state being complete. The results are given in the form of an equilateral triangle diagram. Each temperature of solidification is common to a series of mixtures, both of the three acids and of two of them, and, in order to determine whether a mixture under examination consists of two or three acids, and to ascertain the proportions of each, it is necessary either to estimate the stearic acid by Hehner and Mitchell's method, or to determine the iodine number. It is found that the iodine number corresponds very closely with the proportion of oleic acid in the mixture. The iodine numbers and the temperatures at which crystallisation commences are given for a number of mixtures of fatty acids derived from natural fats and oils.

T. H. P.

Hydrolysis of Fats and Oils. RUDOLF WEGSCHEIDER (*Chem. Zeit.*, 1909, **33**, 1220).—Some remarks on Kellner's paper (Abstr., 1909, i, 759).

Kellner's observations are in harmony with the theory of a gradual saponification.

L. DE K.

Detergent Action of Soap Solutions. Part II. WALTHÈRE SPRING (*Rec. trav. chim.*, 1909, **28**, 424—443).—In the previous paper of this series (Abstr., 1909, i, 628) the detergent action of soap solutions for lampblack was considered, and in the present paper the investigation is extended to ferric compounds, and more especially "red ochre." The conclusions as to the general mode of action of soap, already indicated, are confirmed.

The red ochre employed had the composition represented by the formula $7Fe_2O_3,3H_2O$. As in the case of lampblack, so with ochre (*loc. cit.*), an *optimum* concentration of soap solution exists, from which the rate of deposition of the ochre is a minimum. This concentration is about 0·5%. The colloidal compound formed between soap and ochre is slightly soluble in water, so that all the solutions used retained a red colour even after the deposition of the ochre. Evidence as to the formation of this colloidal compound was obtained by analysis of soap solutions in water or methyl alcohol, in which ochre had been suspended. The ashes from these were less in amount than those from the original soap solutions, showing that a portion of

the soap had been carried out by the ochre. It appears, therefore, that, as with lampblack, the soap is decomposed into a basic portion and an acid portion, the former being carried down by the ochre. The deposition of ochre from suspension in water is accelerated by alkalis or acids so long as more than 0·078% of alkali or more than 0·0001% of acid is present.

Water containing ochre in suspension may be filtered clear eventually by passing it many times through filter paper, but the ochre deposited in such filter paper is again carried through by soap solution. The amount of ochre thus carried through by soap solution does not increase with the concentration of the latter until this falls below 0·25%.

Soap solutions tend to flocculate colloidal solutions of ferric hydroxide, and a minimum molecular concentration (1 mol. soap to 2·16 mols. of ferric oxide) exists, at which turbidity but no precipitation occurs, and a maximum concentration (1 mol. soap to 3·47 mols. of ferric oxide), at and beyond which complete flocculation of the ferric compound takes place. The precipitate formed is yellow in colour, but on drying becomes chocolate-brown, and is a colloidal compound of soap and ferric hydroxide having the formula

$$38Fe_2O_3,9(NaC_{17}H_{33}O_2),71H_2O.$$

It does not adhere to glass, paper, or skin, and is quite different in properties from "ferric soap" prepared in the usual way by double decomposition. The results indicate that the detergent property of soap for ferric hydroxide is due to the formation of a colloidal compound of the two substances, which no longer has the property of adhering to fabrics or tissues. T. A. H.

Hydroxyaliphatic Acids from the Products of the Interaction of Hypochlorous Acid or Chlorine and the Glycerides of Aliphatic Acids of Animal or Vegetable Origin. GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 214154. Compare Abstr., 1909, i, 875).—Instead of preparing the dihydroxyaliphatic acids from the product of the action of chlorine or hypochlorous acid on the fatty acids themselves, their glycerides may be employed, and the hydrolysis of the dichloro- or chlorohydroxyglyceride can be effected at the same time as the replacement of chlorine by hydroxyl.

The glyceride of chlorohydroxystearic acid, obtained by the action of hypochlorous acid on olive oil, was heated with a 7% solution of sodium carbonate at 150°, and the dihydroxystearic acid precipitated with sulphuric acid.

The glyceride of dichlorostearic acid, produced by the action of chlorine on olive oil, is hydrolysed in the same way. F. M. G. M.

Stereochemistry of the Glutaconic Acid Group. FRANZ FEIST (*Annalen*, 1909, **370**, 41—60. Compare Perkin, Trans., 1897, **71**, 1182; 1902, **81**, 246; 1903, **83**, 8, 771).—A theoretical paper devoted to a discussion of the stereoisomerism of alkyl derivatives of glutaconic acid and of the observations recorded in the following abstracts and p. i, 39.

It is found that α-methylglutaconic acid in analogy to β-methylglutaconic acid (compare Feist, Abstr., 1906, i, 334) exists in two stereoisomeric modifications, thus providing another case against the view advanced by Thorpe (Trans., 1905, **87**, 1669). Attempts to prepare two isomeric β-phenylglutaconic acids have been unsuccessful.

Many alkyl derivatives of glutaconic acid have been isolated in one form only, and in cases where the anhydride has been prepared, as, for example, the αγ-dimethyl, β-methyl-α-ethyl, and αβγ-trimethyl derivatives, these compounds have been regarded as the *cis*-modifications. The great stability of these compounds and the impossibility of converting them into the more stable *trans*-isomerides made it appear probable that, notwithstanding the close relationship existing between the acid and its anhydride, the acid might be the *trans*-form produced by the spontaneous transformation of the *cis*-isomeride at the moment of its production from the anhydride. Attempts were made, therefore, to prevent the transformation of the *cis*-compound into the *trans*-form by acting on the anhydride with alkali in the presence of an anti-catalyst, and with success; for example, the anhydride of α-methylglutaconic acid when treated with alkali in the presence of casein and subsequently with silver nitrate yields a silver salt, which, when decomposed by hydrogen sulphide, gives the *cis*-acid, m. p. 118°; in the absence of casein, the *trans*-acid, m. p. 145—146°, containing traces of the *cis*-isomeride, is obtained.

The effect on the stability of the stereo-isomerides produced by the replacement of the various hydrogen atoms of glutaconic acid by alkyl groups may be summarised as follows: (1) Replacement of the two α-hydrogen atoms renders the isomerides very stable; they cannot be converted one into the other; if only one atom is substituted, then the isomerides may with difficulty be transformed one into the other. The effect of alkyl groups in the α-position is neutralised to some extent by substitution of a β- or γ-hydrogen atom; thus, *cis*-ααγ-trimethylglutaconic acid passes quite readily into the *trans*-acid. (2) The compounds obtained by replacing a β- or γ-hydrogen atom by an alkyl group, even if one of the α-hydrogen atoms is likewise replaced by an alkyl group, have been obtained only in the stable *trans*-form, with the exception of β methylglutaconic acid (compare Perkin, Trans., 1902, **81**, 246; Thorpe, Trans., 1905, **87**, 1669; Perkin and Thorpe, Trans., 1898, **71**, 1182).

The readiness with which the glutaconic acids yield anhydrides depends largely on the position of the alkyl groups; in agreement with the results of Victor Meyer and of Auwers, the tendency to form an anhydride is increased by the accumulation of alkyl groups, but it is found that substitution of the β-hydrogen atom leads more particularly to the ready formation of anhydrides; thus, αβγ-trimethylglutaconic acid, αβ-dimethylglutaconic acid, β-phenylglutaconic acid, and β-methylglutaconic acid yield anhydrides when fused, whereas αγ-dimethylglutaconic acid and α-methylglutaconic acid do not yield anhydrides when treated similarly.

The stability of the anhydrides towards the addition of water, likewise the ability of the various glutaconic acids to form additive

products, depends largely on the position of the alkyl group, but rules of general applicability cannot be given. W. H. G.

Stereoisomeric α-Methylglutaconic Acids. FRANZ FEIST and G. POMME (*Annalen*, 1909, **370**, 61—72. Compare preceding abstract). —Ethyl sodiodicarboxyglutaconate when treated with an alcoholic solution of methyl sulphate yields ethyl dicarboxymethylglutaconate, which, when hydrolysed with aqueous alkali or hydrochloric acid, yields a mixture of two isomeric α-methylglutaconic acids, melting at 145—146° and 118° respectively. The acid m. p. 145—146°, first described by Conrad and Guthzeit, is shown to be the *trans*-modification, since α-methylglutaconic anhydride absorbs water from the air, yielding the acid, m. p. 118°, and when treated with alkali in the presence of casein yields the same acid, m. p. 118°; the crystalline *calcium* ($2\frac{1}{2}H_2O$) and *barium* ($2H_2O$) salts were analysed; the acid changes partly into the *cis*-isomeride when treated with dilute hydrochloric acid or aqueous sodium hydroxide.

cis-*α-Methylglutaconic acid*, $C_6H_8O_4$, m. p. 118°, does not alter when fused, but is partly converted into the *trans*-isomeride by hot dilute hydrochloric acid; the *barium* ($2H_2O$) and *calcium* ($4H_2O$) salts were analysed.

α-Methylglutaconic anhydride, $C_6H_6O_3$, cannot be prepared by the action of acetyl chloride or thionyl chloride on the acid, but is obtained by treating the acid with phosphorus pentachloride; it crystallises in long needles, m. p. 85°, and when warmed with aniline yields the *semianilide*, $CO_2H\cdot CHMe\cdot CH\!:\!CH\cdot CO\cdot NHPh$ or

$$CO_2H\cdot CH\!:\!CH\cdot CHMe\cdot CO\cdot NHPh,$$

crystallising in white needles, m. p. 165°.

trans α-Methylglutaconic acid interacts (1) with aniline at 150°, yielding *α-methylglutaconanil*, $CH{<}{\begin{matrix}CHMe\cdot CO\\CH\text{——}CO\end{matrix}}{>}NPh$, which crystallises in needles, m. p. 229°, and (2) with hydrobromic acid in glacial acetic acid, with the formation of *bromo-α-methylglutaconic acid*, $C_6H_9O_4Br$, crystallising in needles, m. p. 141°.

An attempt to prepare α-methylglutaconic acid by reducing ethyl methylacetonedicarboxylate, heating the product with acetic anhydride, and hydrolysing the ester so formed, led to the isolation of a *substance*, $C_{11}H_{14}O_6$, m. p. 141°. W. H. G.

αγ-Dimethylglutaconic Acids. FRANZ FEIST and R. REUTER (*Annalen*, 1909, **370**, 82—92. Compare preceding abstracts; Reformatzky, Abstr., 1899, i, 481; Blaise, Abstr., 1903, i, 400, 548). —The object of this investigation was to prepare a second αγ-dimethylglutaconic acid by making use of casein as an anti-catalyst; this could not be done, however, owing to the impossibility of preparing a normal anhydride of the acid. αγ-Dimethylglutaconic acid does not pass into the anhydride when fused or when heated with acetyl chloride, thionyl chloride, or concentrated sulphuric acid. When warmed with phosphorus pentachloride it yields small quantities of a

substance, $CH<\begin{matrix}CMe-CO\\CMe\cdot CCl\end{matrix}>O$ (?), crystallising in small needles, m. p. 82—83°, and relatively large quantities of a *substance*, the properties of which are most in accord with the formula

$$CH<\begin{matrix}CMe\text{—}CO\cdot C\colon CMe\text{—}CO\\CHMe\cdot CO\cdot CMe\cdot CO\cdot O\end{matrix}.$$

The latter substance forms white crystals, m. p. 207—208°, and undergoes the following changes: (1) when boiled with water it yields the dibasic *acid*, $C_{14}H_{16}O_6$, m. p. 176—176·5° (decomp.); (2) when treated with aniline, it yields the *semianilide*, $CO_2H\cdot C_{12}H_{14}O_2\cdot CO\cdot NHPh$, m. p. 247—248°, and a *substance*, m. p. 151°, obtained as a white powder; (3) it is converted by a solution of sodium methoxide in methyl alcohol into the *methyl hydrogen* ester,

$$CO_2H\cdot C_{12}H_{14}O_2\cdot CO_2Me,$$

a white, crystalline substance, m. p. 183—183·5°, and a crystalline *substance*, $C_{15}H_{20}O_4$, m. p. 142—143°; (4) it combines with bromine, yielding a *dibromo*-derivative, $C_{14}H_{14}O_5Br_2$, m. p. 163°. W. H. G.

Derivatives of Propylsuccinic Acid. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1909, [iv], 5, 1071—1074).—Propylsuccinic acid (m. p. 91—92°) was prepared by Waltz's process (Abstr., 1882, 948), and converted into the anhydride, b. p. 145—150°/13 mm., by heating it, complete transformation being secured by boiling the product with acetic anhydride. The following new derivatives suitable for the identification of the acid are described.

With aniline the anhydride yields the *monoanilide*, m. p. 123—126°, which crystallises from benzene on adding alcohol, and on heating at 180—200° during fifteen minutes passes into the *anil*, m. p. 83°, which crystallises from a mixture of alcohol and light petroleum.

Ethyl propylsuccinate has b. p. 132—134°/25 mm. The methyl ester, b. p. 107°/11 mm. or 112°/15 mm., on treatment with ammonia yields the *diamide*, m. p. 234—235°, which crystallises in colourless needles from alcohol containing acetic acid. With hydrazine hydrate the methyl ester yields the *dihydrazide*, m. p. 176°, which separates from alcohol as a white powder, and condenses with benzaldehyde to give a *dibenzylidene* derivative, m. p. 226°, a white powder, which is difficult to purify by reason of its insolubility in organic solvents.

T. A. H.

Cholic Acid. I. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1909, **63**, 308—312).—When an alkaline solution of dehydrocholic acid (Hammarsten, Abstr., 1881, 624; Mylius, *ibid.*, 1886, 952; 1887, 983) is reduced electrolytically, using lead terminals and a porous cell, the chief product is *reductodehydrocholic acid*, $C_{24}H_{36}O_5$, a compound intermediate between cholic and dehydrocholic acids. The acid crystallises from benzene in minute, colourless needles, m. p. 188°, and yields a *dioxime*, $C_{24}H_{36}O_3(NOH)_2$, which crystallises from alcohol in slender needles decomposing at 254—256°. J. J. S.

American Colophony. PAUL LEVY (*Ber.*, 1909, **42**, 4305—4308).—When sodium abietate from American colophony is oxidised with a 2% solution of potassium permanganate at the ordinary temperature, the products are *tetrahydroxyabietic acid*, propionic acid, *iso*butyric acid, and resins. The tetrahydroxy-derivative, $C_{20}H_{34}O_6$, is separated from the resins by treatment with acetone, when it forms a colourless powder, which crystallises in well-developed crystals, m. p. 246—247° (decomp.). The *silver* salt, $C_{20}H_{33}O_6Ag,2{\cdot}5H_2O$, and *barium* salt,

$$C_{40}H_{66}O_{12}Ba,4H_2O,$$

are described.

The tetrahydroxy-acid is probably identical with Fahrion's tetrahydroxysylvic acid (Abstr., 1901, i, 166), and the formation of the acid is regarded as supporting the author's view that abietic acid contains two ethylene linkings. J. J. S.

Catalytic Preparation of Unsymmetrical Aliphatic Ketones. JEAN B. SENDERENS (*Compt. rend.*, 1909, **149**, 995—997. Compare Abstr., 1909, i, 286, 627).—The method for the preparation of symmetrical ketones already described has now been extended to the production of mixed ketones; thus methyl ethyl ketone is obtained by passing a mixture of the vapours of acetic and propionic acids over thorium dioxide at 400—430°. Acetophenone and acetone are obtained when acetic acid (3 mols.) and benzoic acid (1 mol.) are employed. The separation of the unsymmetrical ketones from the accompanying smaller quantities of symmetrical products is easily effected by fractionation. W. O. W.

Synthesis of Ketones by means of Organo-magnesium Compounds. JULIUS SALKIND and (Madame) T. BEBURISCHWILI (*Ber.*, 1909, **42**, 4500—4502).—The diminution of the reactivity of the carboxyl group towards organo-magnesium compounds, produced by a second carboxyl group (compare Simonis and Arand, Abstr., 1909, i, 932), probably accounts for the formation of esters of β-keto-acids by the action of magnesium on esters of α-bromo-acids (compare Abstr., 1907, i, 22; Zeltner and Reformatsky, Abstr., 1907, i, 23; Salkind and Baskoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 327). In this case the magnesium compound, $MgBr{\cdot}CHR{\cdot}CO_2Et$, formed in the ordinary way, condenses immediately with its own carboxyl group, yielding a product of the formula: $MgBr{\cdot}CHR{\cdot}C(OEt)(OMgBr){\cdot}CHR{\cdot}CO_2Et$, which gives a good yield of a substituted acetoacetic ester when decomposed by means of water. Tertiary hydroxy-acids are never obtained in this way, so that with them, addition of a second molecule of the Grignard compound does not occur.

The authors have investigated the action of Grignard's compounds on the sodium salts of carboxylic acids (compare Grignard, Abstr., 1904, i, 213; Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1906, i, 660). When perfectly dry sodium acetate or propionate is added, with cooling and continual stirring, to the calculated proportion of the organo-magnesium compound, and the mixture decomposed after twenty-four hours by iced water, the ketone is obtained, the yield of crude product being 25—27%. Thus, with magnesium *iso*-

butyl bromide and sodium acetate, methyl *iso*butyl ketone is obtained; with magnesium *iso*amyl iodide and sodium acetate, methyl *iso*amyl ketone; with magnesium phenyl bromide and sodium acetate, acetophenone; and with magnesium ethyl bromide and sodium propionate, diethyl ketone.
T. H. P.

The Hexosephosphate Formed by Yeast-Juice from Hexose and a Phosphate. WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1909, *B*, **81**, 528—545. Compare Abstr., 1905, ii, 109; 1906, i, 470; 1908, ii, 590; 1909, i, 863).—The compound formed during the accelerated fermentation of dextrose, lævulose, and mannose by yeast-juice in the presence of a soluble phosphate is a salt of an acid which probably has the formula $C_6H_{10}O_4(PO_4H_2)_2$, and may be isolated by precipitation of its lead salt. The free acid may be obtained in solution by decomposing this lead salt with hydrogen sulphide. The acid is very unstable, and readily decomposes on keeping, or on evaporating even at the ordinary temperature in a vacuum over sulphuric acid, with formation of a reducing substance and phosphoric acid. It reduces Fehling's solution, but no osazones or hydrazones have been obtained from it. No differences have been detected between the hexosephosphoric acids or their salts, whether derived from dextrose, lævulose, or mannose. The salts of lead, barium, silver, and cadmium have been prepared.
G. S. W.

Platinum. ALEXANDER GUTBIER and FR. BAURIEDEL (*Ber.*, 1909, **42**, 4243—4249. Compare Abstr., 1903, ii, 488).—In connexion with the revision of the atomic weight of platinum, the authors have prepared a number of substituted ammonium salts of hydrogen platinibromide. A solution of hydrogen platinichloride was evaporated on the water-bath six times with concentrated hydrobromic acid. The residue was then treated several times in a similar manner with hydrobromic acid containing bromine, and the final residue dissolved in dilute hydrobromic acid. In this way a dark carmine-red solution was obtained, from which crystals of hydrogen platinibromide, $H_2PtBr_6,9H_2O$, separated on evaporation over lime. By the addition of solutions of substituted ammonium bromides to this solution, the following platinibromides were precipitated in a pure condition.

Methylammonium platinibromide, $(NH_3Me)_2PtBr_6$: light brown to reddish-brown, six-sided, regular plates, which are still solid at 260°.

Dimethylammonium platinibromide, $(NH_2Me_2)_2PtBr_6$: slender, red, rhombic prisms, m. p. 232° (decomp.). *Trimethylammonium platinibromide*, $(NHMe_3)_2PtBr_6$: dark red octa- and hexa-hedra, m. p. 253—254° (decomp.). *Ethylammonium platinibromide*, $(NH_3Et)_2PtBr_6$: yellowish-red, six-sided, regular plates, which are still solid at 264°. *Diethylammonium platinibromide*, $(NH_2Et_2)_2PtBr_6$, monoclinic plates, m. p. 251—252° (decomp.). *Triethylammonium platinibromide*, $(NHEt_3)_2PtBr_6$: ruby-red crystals, probably monoclinic, m. p. 231—232°. n-*Propylammonium platinibromide*, $(NH_3Pr^{\alpha})_2PtBr_6$, red, monoclinic plates, m. p. 257—258° (decomp.). iso*Propylammonium platinibromide*, $(NH_3Pr^{\beta})_2PtBr_6$: yellowish-red, six-sided plates, m. p.

267°. *n-Butylammonium platinibromide*, $(C_4H_9 \cdot NH_3)_2PtBr_6$: yellowish-red, six-sided plates, m. p. 256°. iso*Butylammonium platinibromide*, $(C_4H_9 \cdot NH_3)_2PtBr_6$: ruby-red, monoclinic prisms, m. p. 266°. *Ethylenediammonium platinibromide*, $C_2H_{10}N_2PtBr_6$: red, six-sided prisms, which remain solid at 270°. *Propylenediammonium platinibromide*, $C_3H_{12}N_2PtBr_6$: dark red prisms, which are still solid at 270°.

T. S. P.

Preparation of Hydroxamic Acids from Hydroxylamine Salts of Organic Acids. LAUDER WILLIAM JONES and RALPH OESPER (*Amer. Chem. J.*, 1909, **42**, 515—520).—When hydroxylamine formate (Sabenéeff, Abstr., 1900, ii, 14), m. p. 76°, is left for several weeks at the ordinary temperature, or heated for a few minutes at its m. p., it is partly converted into formhydroxamic acid. If, however, the salt is heated above 80°, violent decomposition occurs. The reaction is reversible, and it is shown that formhydroxamic acid can be synthesised by treating hydroxylamine with dry carbon monoxide. When hydroxylamine acetate is heated at 90° in a sealed tube, acethydroxamic acid is produced in a yield of about 25—30%. Preliminary experiments have shown that hydroxylamine benzoate and anisate also yield the corresponding hydroxamic acids when heated slightly above their m. p.'s. E. G.

Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates. ARTHUR ROSENHEIM (*Ber.*, 1909, **42**, 4439—4440). —Polemical. A reply to Hantzsch (Abstr., 1909, i, 894; compare Rosenheim, Levy, and Grünbaum, *ibid.*, i, 776). R. V. S.

Dithiourethanes. II. Preparation of Thioglycols from Bisdithiourethanes. JULIUS VON BRAUN (*Ber.*, 1909, **43**, 4568—4574. Compare Abstr., 1902, i, 271).—The behaviour of dihalogen substituted aliphatic hydrocarbons towards dithiocarbamates has been studied to test the influence of the distance between the halogens on the introduction of the thiourethane complex. The reaction between $\omega\omega'$-di-iodo-ethane, -propane, -butane, -pentane, -hexane, and -decane and a dithiocarbamate takes place readily and with equal velocity at both ends of the molecule, forming only bisdithiourethanes, $NR_2 \cdot CS \cdot S \cdot [CH_2]_x \cdot S \cdot CS \cdot NR_2$, and never iododithiourethanes,

$$NR_2 \cdot CS \cdot S \cdot [CH_2]_x \cdot I.$$

The products are indifferent substances; the *piperidine* derivatives, $C_5NH_{10} \cdot CS \cdot S \cdot [CH_2]_x \cdot S \cdot CS \cdot C_5NH_{10}$, have been analysed. They crystallise remarkably well, and the melting point only slowly falls with an increase in the length of the chain. The *propane* derivative has m. p. 140°; *butane* derivative, m. p. 125°; *pentane* derivative, m. p. 103°; *hexane* derivative, m. p. 94°; *decane* derivative, m. p. 90°.

The di-iodo-compounds interact similarly with carbon disulphide and primary amines, but the dithiourethanes formed are more soluble, and were only obtained as viscid oils which decompose when warmed.

On mixing finely powdered ammonium dithiocarbamate with the di-iodo-compounds in alcoholic solution, a colourless precipitate

gradually forms; the time of formation of this does not seem to depend on the molecular weight of the iodide. The bisdithiourethanes formed were not obtained quite pure, and did not show sharp melting points. They softened from 100° to 150°. When warmed with potassium hydroxide, they are converted into the corresponding thioglycols.

Butylene αδ-dithiol, $HS\cdot[CH_2]_4\cdot SH$, is a colourless oil, b. p. 105—106°/30 mm.; the *benzoyl* derivative forms long needles, m. p. 49°.

Hexylene αζ-dithiol, $HS\cdot[CH_2]_6\cdot SH$, has b. p. 118—119°/15 mm.; the *benzoate* has m. p. 57°.

Decalene ακ-dithiol has b. p. 176°/16 mm., m. p. 20°; the *benzoate* has m. p. 55°. It is almost without odour. E. F A.

Compounds from Guanylcarbamide and Diguanide. JULIUS SOLL and ALBERT STUTZER (*Ber.*, 1909, **43**, 4532—4541).—On evaporating dicyanodiamide with mineral acids, salts of guanylcarbamide are obtained, from which the free base has been prepared. To prepare dicyanodiamide, crude commercial cyanamide is stirred to a paste with water, boiled, and filtered hot; the dicyanodiamide crystallises from the filtrate. When evaporated with sulphuric acid, *guanylcarbamide hydrogen sulphate*, $NH:C(NH_2)\cdot NH\cdot CO\cdot NH_2,H_2SO_4$, is formed, which when decomposed with barium hydroxide gives guanylcarbamide. This crystallises from alcohol $+C_2H_6O$ in lustrous, glass-like prisms, which very rapidly take up carbon dioxide from the air. The alcohol evaporates in a desiccator. The free base has m. p. 105°; it evolves ammonia at 160°, or on boiling with water. The *picrate* crystallises in yellow plates, m. p. 265° to a clouded, yellow mass, decomp. 285°; it may be used to estimate guanylcarbamide quantitatively. The heat of combustion of guanylcarbamide nitrate is 327·4 Cal. Guanylcarbamide condenses readily in alcoholic solution, forming pyrimidine bases.

Guanylcarbamidesulphonic acid, $C_2H_5ON_4\cdot SO_3H$, is obtained by heating guanylcarbamide sulphate with acetic anhydride; it crystallises in prisms, decomp. 220—230°; the *ammonium* salt forms short, thick prisms, m. p. 165—167°; the *barium* and *calcium* salts are similar. Acetic anhydride and sulphuric acid convert the sulphonic acid into acetylguanylcarbamide.

Acetylsulphuric acid acts on acetanilide to form acetylsulphanilic acid, crystallising in long needles from acetic acid (compare Schröter, Abstr., 1906, i, 415).

Guanylcarbamide condenses with monochloroacetic acid on heating to guaninoacetic acid (Ramsay, Abstr., 1909, i, 88). It forms a picrate crystallising in plates, m. p. 235—237°, differing from that described by Ramsay, m. p. 201° (*loc. cit.*). The new guaninoacetic acid is probably bimolecular; when boiled with hydrogen chloride, the hydrochloride of unimolecular guaninoacetic acid is formed, which gives the picrate, m. p. 202°. E. F. A.

Action of Hydrogen Chloride on Acetone Cyanohydrin. A. J. ULTÉE (*Rec. trav. chim.*, 1909, **28**, 349—353. Compare Pinner, Abstr., 1884, 1292).—When dry hydrogen chloride is passed into

acetone cyanohydrin, cooled to 0°, two condensation products are formed.

The first of these is an *imino-ether hydrochloride*,

$$C_8H_{14}O_2N_2,HCl,H_2O,$$

m. p. 231° (decomp.), and remains undissolved when the reaction product is mixed with rather less than its own volume of water. It is readily soluble in water, is precipitated therefrom by hydrochloric acid, and, on addition of alkalis, yields the *imino-ether*, which does not melt even at 280°, and on boiling with excess of alkali dissolves with evolution of ammonia, but, unlike most substances of this class, is not decomposed by water. The formula $HO\cdot CMe_2\cdot C(NH)\cdot O\cdot CMe_2\cdot CN$ or $HN{:}C{<}{\begin{smallmatrix}O\cdot CMe_2\\ CMe_2\cdot O\end{smallmatrix}}{>}C{:}NH$ is provisionally assigned to this substance.

The second *product*, $C_{12}H_{19}O_5N$, m. p. 193°, separates almost at once in colourless crystals from that part of the reaction mixture which is miscible with water. It is slightly soluble in water, readily so in chloroform, acetone, or alkalis, but is precipitated from solutions in alkalis by acids. When boiled with alkalis, it evolves ammonia, and on long boiling with hydrochloric acid forms *a-iso*butyric acid. The following formula is provisionally assigned to this product:

$$\begin{matrix}O\text{—}CMe_2\cdot CO\cdot NH\\ |\qquad\qquad\qquad\\ CMe_2\cdot CO\cdot O\cdot CMe_2\end{matrix}{>}CO.$$

T. A. H.

Constitution and Behaviour of Semicarbazidesemicarbazones. HANS RUPE and SIDONIUS KESSLER (*Ber.*, 1909, **42**, 4503—4510).—Mesityl oxide semicarbazidesemicarbazone,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

obtained in the form of the hydrochloride by the gradual action of semicarbazide hydrochloride on mesityl oxide, is stable in dilute aqueous alkalis, giving solutions which reduce ammoniacal silver nitrate and Fehling's solutions; the *hydrochloride*, $C_8H_{19}O_2N_6Cl$, forms microscopic, white needles, m. p. 211—212° (decomp.).

When a solution of the above semicarbazidesemicarbazone in dilute hydrochloric acid is treated with benzaldehyde, the semicarbazide residue united by a double linking to the carbon atom of the ketonic group is removed and benzaldehydesemicarbazone formed, together with diacetonesemicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot CMe_2\cdot CH_2\cdot COMe$, which can be separated as a nitroso-derivative. If the aqueous solution containing diacetonesemicarbazide hydrochloride is left for some time and then extracted with ether, the latter contains the compound obtained (1) by Scholtz (Abstr., 1896, i, 343) by distilling mesityl oxide semicarbazone; (2) by Harries and Kaiser (Abstr., 1899, i, 637) by the direct action of semicarbazide hydrochloride on mesityl oxide, and (3) by Rupe and Schlochoff (Abstr., 1904, i, 144) by boiling mesityl oxide semicarbazidecarbazone with water. This compound, m. p. 131°, being formed from diacetonesemicarbazide, cannot be represented by the first of the two formulæ given by Harries and Kaiser (*loc. cit.*), although the evidence is insufficient to establish the accuracy of the second formula. In aqueous solution the compound reduces gold chloride in the cold and ammoniacal silver solution on

heating; by 10—15% sodium hydroxide solution it is only slowly and sparingly decomposed, with evolution of ammonia, and boiling with acids does not result in the removal of a $\cdot CO\cdot NH_2$ group. With nitrous acid, it yields mesityl oxide and carbamineazoimide (Thiele and Stange, Abstr., 1895, i, 252), which can arise only from a semicarbazone or from free semicarbazide, so that the ring-compound would appear to have been first resolved.

Nitrosodiacetonesemicarbazide,

$$NH_2\cdot CO\cdot NH\cdot N(NO)\cdot CMe_2\cdot CH_2\cdot COMe,$$

prepared by the action of nitrous acid on diacetonesemicarbazide, or, together with carbamineazoimide, by the action of nitrous acid (2 mols.) on mesityl oxide semicarbazidesemicarbazone (1 mol.), forms white, rectangular plates, m. p. 145—146° (decomp.), gives Liebermann's reaction, is partly decomposed by water or mineral acids, forming azoimide, and when heated above its m. p. yields nitrogen, nitric oxide, carbon dioxide, ammonia, and azoimide. With semicarbazide (1 mol.) it gives *nitrosodiacetonesemicarbazidesemicarbazone*, $NH_2\cdot CO\cdot NH\cdot N(NO)\cdot CMe_2\cdot CH_2\cdot CMe\!:\!N\cdot NH\cdot CO\cdot NH_2$, which forms small, white needles, m. p. 158°. By alkali in the cold, nitrosodiacetonesemicarbazide is slowly decomposed according to the scheme:

$$\begin{matrix} CMe_2\cdot CH_2\cdot COMe \\ | \\ NO\cdot N\cdot NH\cdot CO\cdot NH_2 \end{matrix} = CMe_2\!:\!CHAc + NO\cdot NH\cdot NH\cdot CO\cdot NH_2 \longrightarrow$$

$$\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!N\cdot CO\cdot NH_2 + H_2O \longrightarrow N_3H + CO_2 + NH_3.$$

When nitrosodiacetonesemicarbazide is dissolved in concentrated hydrochloric acid, acetic acid, 40% phosphoric acid, or acetic anhydride, and the solution subsequently diluted and treated with semicarbazide hydrochloride and potassium acetate, a *compound*, $C_6H_{11}O_2N_4$, forming aggregates of slender needles, m. p. 172°, is obtained, which is decomposed by water or dilute sulphuric acid, giving azoimide, and by dilute hydrochloric acid, yielding benzaldehydesemicarbazone. T. H. P.

Metallic Derivatives of Chloro- and Bromo-acetylene. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, **42**, 4232—4238. Compare Abstr., 1908, i, 145).—Mercury tribromoethylene, $Hg(CBr\!:\!CBr_2)_2$, crystallises in well-developed monoclinic prisms [$a : b : c = 1\cdot4829 : 1 : 0\cdot5637$; $\beta = 105°26'$].

Mercury chloroacetylide, $Hg(C\!:\!CCl)_2$, obtained by shaking *s*-dichloroethylene with mercuric cyanide and aqueous potassium hydroxide solution, crystallises in thin, quadratic plates. The crystals exhibit strong double refraction, and decompose at 195°. When mixed with an ethereal solution of iodine and exposed to sunlight, the mercury compound yields *chlorotri-iodoethylene*, $CClI\!:\!CI_2$, which crystallises in long plates, m. p. 78—80°.

Mercury bromoacetylide, $Hg(C\!:\!CBr)_2$, can be prepared from dibromoethylene and an alkaline solution of mercuric cyanide, or by passing the gases, obtained by the action of alcoholic potassium hydroxide on tribromoethylene, into an alkaline solution of mercuric cyanide. It crystallises in thin, rectangular plates, which decompose at 153—155°, and detonate when rubbed on a porous plate. It is volatile

in steam, and is decomposed by boiling with dilute hydrochloric acid or potassium cyanide solution, yielding bromoacetylene. It readily forms an additive compound with mercuric bromide in the form of an amorphous powder. Pure chloro- and bromo-acetylene are readily prepared by warming the respective mercury compounds with potassium cyanide solution, care being taken that the air in the apparatus is replaced by hydrogen. When chloroacetylene is passed into ammoniacal silver nitrate solution, a white precipitate of AgC⋮CCl is formed. This darkens rapidly on exposure to sunlight, and is more explosive than silver acetylide. The corresponding explosive copper derivative has also been prepared.

Chloroacetylene mixed with hydrogen reacts with a saturated aqueous solution of mercuric chloride, yielding *trichloromercuriacetic acid*, $C(HgCl)_3 \cdot CO_2H$ (compare Abstr., 1905, i, 2), in the form of a crystalline powder, which is decomposed by hydrochloric acid, forming mercuric chloride and acetic acid. The acid dissolves in cold dilute potassium hydroxide solution, but, when heated, polymeric mercuriacetic acid is precipitated. When chloroacetylene is led into a solution of mercuric chloride and sodium acetate, a precipitate of *dichloromonohydroxy-trimercuriacetic acid*, $OH \cdot Hg \cdot C(HgCl)_2 \cdot CO_2H$, is obtained. When dissolved in cold dilute potassium hydroxide solution and precipitated with carbon dioxide, *tri-hydroxymercuriacetic acid*,

$$C(Hg \cdot OH)_3 \cdot CO_2H,$$

is obtained as a yellowish-white powder.

When mercury chloroacetylide is shaken with a solution of mercuric chloride and sodium acetate, a *precipitate*, $C_4H_2O_2Cl_4Hg_3$, is thrown down. J. J. S.

Halogen-amino-acids. VI. Iodo-derivatives of *p*-Toluidine. 3 : 5-Di-iodo-4-aminobenzoic Acid. HENRY L. WHEELER and LEONARD M. LIDDLE (*Amer. Chem. J.*, 1909, **42**, 441—461).—The only iodo-derivatives of *p*-toluidine hitherto described are the 2-iodo-derivative (Willgerodt and Gartner, Abstr., 1908, i, 876) and a di-iodo-derivative (Michael and Norton, Abstr., 1878, 407), which was regarded as the 3 : 5-compound. The corresponding di-iodo-derivative of *p*-aminobenzoic acid was also obtained by the latter authors. A study has now been made of these di-iodo-derivatives, and several other compounds have been prepared.

3-*Iodo*-p-*toluidine*, $NH_2 \cdot C_6H_3MeI$, m. p. 40°, obtained by the interaction of molecular proportions of iodine and *p*-toluidine, forms colourless needles; the *hydrochloride*, m. p. 188° (decomp.), and the *oxalate*, m. p. 119—120° (decomp.), are described. The *acetyl* derivative, m. p. 133°, crystallises in long, colourless prisms, and, when boiled with concentrated hydrochloric acid, yields 3 : 5-di-iodo-*p*-toluidine. The *benzoyl* derivative, m. p. 161°, forms long, colourless needles.

3-*Iodo*-p-*tolylcarbamide*, m. p. 187°, prepared by the action of potassium cyanate on 3-iodo-*p*-toluidine, forms thin, colourless plates. When 3-iodo-*p*-toluidine is heated with potassium thiobenzoate, benzenyl-4-amino-3-thiocresol (Hesse, Abstr., 1881, 597) is produced; its *platinichloride* crystallises with $1H_2O$.

3-*Iodo*-5(?)-*nitroaceto*-p-*toluidide*, $NO_2\cdot C_6H_2MeI\cdot NHAc$, m. p. 202—203°, obtained by the action of nitric acid on 3-iodoaceto-*p*-toluidide, crystallises in prisms.

When *p*-toluidine (1 mol.) is warmed with iodine (2 mols.) in presence of water and calcium carbonate, 3 : 5-di-iodo-*p*-toluidine (Michael and Norton, *loc. cit.*) is produced; its *acetyl* derivative, m. p. 226°, forms stout, colourless prisms. 3 : 5-*Di-iodotoluene*, m. p. 44·5—45·5°, obtained by diazotising 3 : 5-di-iodo-*p*-toluidine in alcoholic solution and boiling the product, crystallises in yellow needles. 3 : 4 : 5-*Tri-iodotoluene*, m. p. 122—123°, prepared by the diazotisation of 3 : 5-di-iodo-*p*-toluidine dissolved in concentrated sulphuric acid, forms long, silky needles.

2-*Iodo*-3-*nitrotoluene*, $NO_2\cdot C_6H_3MeI$, m. p. 67—68°, obtained by treating the product of the diazotisation of 3-nitro-*o*-toluidine with potassium iodide, crystallises in light yellow plates, and, on reduction with ferrous sulphate and ammonia, is converted into 2-*iodo*-m-*toluidine*, m. p. 41—42°, which forms long, flat prisms and yields an *acetyl* derivative, m. p. 135°. When the product of the diazotisation of 2-iodo-*m*-toluidine is treated with potassium iodide, 2 : 3-*di-iodotoluene*, m. p. 31—32°, is produced, which crystallises in colourless plates.

3-*Iodo*-4-*acetylaminobenzoic acid*, m. p. 230°, obtained by the oxidation of 3-iodoaceto-*p*-toluidide with potassium permanganate, forms long, colourless prisms. 2-*Iodo*-3-*acetylaminobenzoic acid*, m. p. 199°, prepared in a similar manner from 2-iodoaceto-*m*-toluidide, crystallises in prismatic needles. When 3-iodo-4-acetylaminobenzoic acid is boiled with concentrated hydrochloric acid, a mixture of *p*-aminobenzoic acid and 3 : 5-di-iodo-4-aminobenzoic acid is produced, the latter agreeing in properties with the compound obtained by Michael and Norton (*loc. cit.*) by the action of iodine monochloride on *p*-aminobenzoic acid. This compound can also be obtained, but only in poor yield, by the oxidation of 3 : 5-di-iodoaceto-*p*-toluidide with permanganate; its *ethyl* ester melts at 148°. 3-*Iodo*-4-*aminobenzoic acid*, m. p. 201—202°, is formed as an intermediate product in the preparation of 3 : 5-di-iodo-4-aminobenzoic acid by boiling 3-iodo-4-acetylaminobenzoic acid with hydrochloric acid, but is best prepared by the action of iodine monochloride on *p*-aminobenzoic acid. When potassium *p*-aminobenzoate is treated with iodine, *p*-iodoaniline is formed, but 3-iodo-4-aminobenzoic acid is not obtained. By the action of iodine on potassium 3 : 5-di-iodo-4-aminobenzoate, tri-iodoaniline, m. p. 184°, is produced.

3 : 4-*Di-iodobenzoic acid*, m. p. 257°, obtained by the action of potassium iodide on the product of the diazotisation of 3-iodo-4-aminobenzoic acid, crystallises in needles.

3 : 5-*Di-iodobenzoic acid*, m. p. 235°, prepared by the diazotisation of 3 : 5-di-iodo-4-aminobenzoic acid, forms pale yellow prisms.

3 : 4 : 5-*Tri-iodobenzoic acid*, m. p. 288°, obtained by adding potassium iodide to the product of the diazotisation of 3 : 5-di-iodo-4-aminobenzoic acid, crystallises in prismatic needles; its *sodium* salt crystallises with $2\frac{1}{2}H_2O$. 3 : 5-Di-iodo-4-hydroxybenzoic acid was also obtained from 3 : 5-di-iodo-4-aminobenzoic acid by means of the diazo-

reaction, but can be most conveniently prepared by the addition of iodine to a solution of *p*-hydroxybenzoic acid in potassium hydroxide. When dipotassium 3 : 5-di-iodo-4-hydroxybenzoate is heated with methyl iodide, *methyl* 3 : 5-*di-iodo*-p-*anisate*, m. p. 95°, is produced. 3 : 5-*Di-iodo*-p-*anisic acid*, m. p. 255—256° (decomp.), forms colourless prisms. E. G.

Halogen-amino-acids. VII. Iodine Derivatives of *o*-Toluidine. 3-Iodoaminobenzoic Acids. HENRY L. WHEELER and LEONARD M. LIDDLE (*Amer. Chem. J.*, 1909, **42**, 498—505).—In an earlier paper (preceding abstract), it has been shown that by the action of iodine on *p*-toluidine, the 3-iodo- and 3 : 5-di-iodo-derivatives can be obtained.

A study has now been made of the action of iodine on *o*-toluidine, and it has been found that in this case only one derivative, namely, the 5-iodo-derivative (Artmann, Abstr., 1905, i, 879), is formed, and that this can be melted with iodine without further substitution being effected.

2 : 5-*Di-iodotoluene*, m. p. 30—31°, obtained by the action of potassium iodide on the product of the diazotisation of 5-iodo-*o*-toluidine, forms long, colourless plates; its *acetyl* derivative, m. p. 169°, and *benzoyl* derivative, m. p. 184°, crystallise in colourless needles. By the oxidation of the acetyl derivative with potassium permanganate, 5-*iodo*-2-*acetylaminobenzoic acid*, m. p. 235° (decomp.), is produced, which forms colourless needles, and, when warmed with hydrochloric acid, is converted into 5-iodo-2-aminobenzoic acid, m. p. 209—210°, which is identical with Grothe's β-iodoaminobenzoic acid (Abstr., 1879, 378). It follows from this that Grothe's α-iodoamino- and α-iodonitro-benzoic acids are the 3-iodo-2-amino- and 3-iodo-2-nitro-derivatives and that his β-iodonitrobenzoic acid is the 5-iodo-2-nitro-compound. 3-*Iodo*-5-*nitrobenzoic acid*, m. p. 167°, prepared from 3-amino-5-nitrobenzoic acid (Hübner, Abstr., 1884, 315) by means of the diazo-reaction, forms long, slender, pale yellow needles; this compound is not identical with Grothe's γ-iodonitrobenzoic acid (*loc. cit.*), and the latter must therefore be the 3-iodo-4-nitro-derivative. 3-*Iodo*-5-*aminobenzoic acid*, m. p. 197°, obtained by reducing 3-iodo-5-nitrobenzoic acid with ferrous sulphate and ammonia, forms long, pale yellow crystals; its *hydrochloride* has been prepared. On adding potassium iodide to the product of the diazotisation of 3-iodo-5-aminobenzoic acid, 3 : 5-di-iodobenzoic acid is produced, identical with that obtained by the authors (*loc. cit.*) from 3 : 5-di-iodo-4-aminobenzoic acid. E. G.

Nitration of Diethylaniline. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 297—303. Compare Abstr., 1900, i, 214).—A method of obtaining 3 : 4-dinitrodiethylaniline, 2 : 4-dinitrodiethylaniline, and 2 : 5-dinitrodiethylaniline from diethylaniline is described in detail.

3 : 4-*Dinitrodiethylaniline*, m. p. 95°, exists in a labile, yellow modification and a stable, orange form, also in an extremely labile, yellow form. It is converted by nitric acid (D 1·37) into 2 : 4 : 5-*trinitro-*

diethylaniline, m. p. 158°; if the nitric acid employed contains nitrous acid, then 2 : 4 : 5-*trinitroethylaniline*, m. p. 175°, is formed; the latter substance may also be prepared from the diethyl compound by treatment with sulphuric acid and sodium nitrite.

2 : 5-*Dinitrodiethylaniline* forms red crystals, m. p. 76°.

W. H. G.

Colour and Constitution. ALFRED WERNER (*Ber.*, 1909, 42, 4324—4328).—The author discusses the nature of the linking whereby highly coloured additive compounds are formed from polynitro-compounds and aromatic hydrocarbons or aromatic bases. The part played by the polynitro-compound in the formation of the additive-compound may be attributable to (*a*) hydrogen, either hydroxylic (in nitrophenols) or nuclear (in trinitrobenzene, picryl chloride, etc.), (*b*) the benzene nucleus, in virtue of its unsaturated character, (*c*) the nitro-group. The first alternative is improbable, since colourless trinitromesitylene forms coloured additive compounds. The second is negatived by the fact that chloropicrin and tetranitromethane form coloured compounds with aromatic hydrocarbons and amines. Since the formation of the labile additive compounds cannot be determined by the principal valencies of the nitro-group, the important conclusion is drawn that the appearance of the colour must be conditioned in some way by the supplementary valencies of the nitro-group.

With regard to the influence of the aromatic hydrocarbon in the production of the coloured additive compound, it is shown that tetranitromethane dissolves unsaturated aliphatic hydrocarbons and also unsaturated aliphatic acids (excepting those containing the double linking in the α-position to the carboxyl group) with a yellow colour, whilst the paraffin hydrocarbons, and also stearic acid, form colourless solutions. Consequently the formation of the additive compound is connected with the unsaturation of a hydrocarbon; as far as can be judged at present, the intensity of the colour of the additive compound increases with the unsaturation of the hydrocarbon.

The additive compounds of nitro-compounds and hydrocarbons, therefore, are molecular compounds, the formation of which depends on saturation of the supplementary valencies between nitro-groups and unsaturated carbon atoms.

From the fact that tetranitromethane develops an intense dark brown coloration with trimethylamine, the author draws the conclusion that in the additive compounds of polynitro-compounds and amines the nitro-group is joined, not to unsaturated carbon atoms, but to the tervalent nitrogen. C. S.

Electrolytic Reduction of 2-Nitrotoluene-4-sulphonyl Chloride. FRITZ FICHTER and WALTER BERNOULLI (*Ber.*, 1909, 42, 4308—4311).—Aromatic sulphonyl chlorides containing a nitro-group are reduced much more smoothly than the compounds described previously (Abstr., 1907, i, 690), because the nitro-group is first reduced to an amino-group, and the resulting basic substance readily

dissolves in the cathodic acid liquor. Thus a suspension of 2-nitrotoluene-4-sulphonyl chloride in alcoholic sulphuric acid is readily reduced at a lead cathode below 20°, using a current density of 0 07 amperes per sq. cm., and one and a-half times the quantity of electricity theoretically required. The product is 2-*aminotolyl* 4-*mercaptan sulphate*, which readily changes to the *sulphate* of 2-aminotolyl 4-disulphide by keeping in a loosely closed vessel. 2-*Aminotolyl* 4-*disulphide*, m. p. 82°, forms almost colourless needles, and yields an *acetyl* derivative, m. p. 239°. C. S.

Nitration. VI. Nitroaniline Derivatives of Organic Acids. J. BISHOP TINGLE and C. E. BURKE (*J. Amer. Chem. Soc.*, 1909, 31, 1312—1319).—By the nitration of various *N*-acylanilides, Tingle and Blanck (Abstr., 1908, i, 778, 893) have prepared a large number of substances, the constitutions of some of which were not ascertained at the time, since their determination offered considerable difficulty. The present work was undertaken for the purpose of elucidating the structure of these compounds. Two series of experiments have been carried out; in the first series, *o*-, *m*-, and *p*-nitroanilines were treated at the ordinary temperature with various organic acids in presence of a solvent, whilst in the second series the mixture of acid and nitroaniline was fused, and the heating continued until the reaction was complete. The acids employed were formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic, and picric acids. The nitration products of propionanilide were also investigated.

The product obtained by the nitration of propionanilide with nitric acid or a mixture of nitric and acetic acids has proved to be unchanged propionanilide, whilst the substance obtained by the action of a mixture of nitric and sulphuric acids is p-*nitropropionanilide*, m. p. 182°, which forms yellowish-brown plates.

Stearic acid does not unite with any of the nitroanilines; the products obtained by Tingle and Blanck in their attempts to nitrate stearanilide consisted of impure stearanilide.

Oxalic acid does not combine with the nitroanilines. The substances obtained by the action of nitric acid on oxalanilide prove to be impure oxalanilide. The yellow substance, prepared by the action of a mixture of nitric and oxalic acids on oxalanilide, was p-*nitro-oxalanilide*, m. p. 265°.

Succinic acid does not react with *o*- or *p*-nitroanilines, but on adding the acid to melted *m*-nitroaniline, m-*nitrosuccinylphenylimide*,

$$\begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{matrix} \!\!>\! N\cdot C_6H_4\cdot NO_2,$$

m. p. 172°, is obtained, which forms pale yellow crystals. The compound obtained by Tingle and Blanck on nitrating succinanil was the unchanged anil, whilst the compound prepared by the action of a mixture of nitric and oxalic acids on succinanilide was a *dinitro*-derivative, m. p. 240—243°.

Tartaric acid does not yield a compound with *o*-nitroaniline, but with *m*-nitroaniline it gives m-*nitroaniline* m-*nitrophenyltartramate*,

$NO_2\cdot C_6H_4\cdot NH_2,NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$, m. p. 172°, in the form of small, yellow crystals, and with *p*-nitroaniline it gives p-*nitrophenyltartramic acid*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO_2H,$$

m. p. 218°, which forms bright yellow crystals. The compound obtained by Tingle and Blanck from tartranilide and a mixture of nitric and oxalic acids is found to be s-m-*dinitrotartranilide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2,$$

m. p. 224°.

Citric acid does not give derivatives with *o*- and *p*-nitroanilines, but with the *m*-compound yields a *di*-m-*nitroaniline citrate*, m. p. 207°. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on citranilide is *citryl tris*-m-*nitroanilide*, $C_3H_5O(CO\cdot NH\cdot C_6H_4\cdot NO_2)_3$, m. p. 122°. The other products obtained by the action of nitric acid on citranilide consisted of the impure anilide.

Salicylic and phthalic acids do not react with any of the nitroanilines. Benzoic acid yields small quantities of compounds when fused with *o*- and *m*-nitroaniline, but these have not been identified.

Picric acid does not react with *o*-nitroaniline, but yields the picrates of the meta- and para-isomerides, which have m. p. 147° and 100° respectively. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on picranilide is a *tetranitrodiphenylamine*, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$, m p. 197—200°; by the action of nitric acid on diphenylamine, another *tetranitrodiphenylamine*, m. p. 275°, is produced. E. G.

d-Leucyl-l-tryptophan. HANS FISCHER (*Ber.*, 1909, **42**, 4320—4322).—Formyl-*l*-leucine is converted by Fischer's method (Abstr., 1906, i, 808) into *l*-bromo*iso*hexoic acid, and this by phosphorus pentachloride into *l*-bromo*iso*hexoyl chloride, which is condensed with tryptophan (Abderhalden and Kempe, Abstr., 1907, i, 652) to form l-*bromo*iso*hexoyltryptophan*. This oily product is dissolved in 25% ammonium hydroxide, whereby d-*leucyl*-l-*tryptophan*,

$$C_8H_6N\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH(NH_2)\cdot C_4H_9,$$

is obtained in needles. The dipeptide does not show the biuret reaction, has a sweet taste, is precipitated from acid solutions by phosphotungstic acid, and has $[\alpha]_D^{20}$ $-68\cdot97°$ in *N*-hydrochloric acid. It melts at 189° (corr.), but immediately crystallises to a substance, probably a tautomeride, melting at 225—230°, which can also be produced by crystallising the dipeptide from water, alcohol, and ether. Prepared by the latter method, the *substance*, $C_{17}H_{23}O_3N_3$, darkens at 230°, and has m. p. 243°; in *N*-hydrochloric acid it has $[\alpha]_D^{20}$ $-73\cdot27°$.

C. S.

Maleic and Fumaric Derivatives of *p*-Aminophenols. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 312—326).—The theoretical part of this paper has been already published (Abstr., 1908, i, 783), the author now giving the following experimental results.

p-*Hydroxyphenylmaleinamic acid*, $OH{\cdot}C_6H_4{\cdot}N{:}C(OH){\cdot}CH{:}CH{\cdot}CO_2H$, prepared from *p*-aminophenol and maleic anhydride, separates in crusts of slender, yellow needles or in greenish-yellow prisms, m. p. 182°, and gives no coloration with ferric chloride.

p-*Methoxyphenylmaleinamic acid*, $OMe{\cdot}C_6H_4{\cdot}N{:}C(OH){\cdot}CH{:}CH{\cdot}CO_2H$, prepared from *p*-anisidine and maleic anhydride, crystallises in canary-yellow, dichroic needles or in yellow prisms exhibiting slight greenish-yellow pleochroism, m. p. 180—181°, and with ferric chloride gives a yellowish-brown coloration changing to violet.

p-*Ethoxyphenylmaleinamic acid*, $OEt{\cdot}C_6H_4{\cdot}N{:}C(OH){\cdot}CH{:}CH{\cdot}CO_2H$, prepared from *p*-phenetidine and maleic anhydride, crystallises in spherical aggregates of slender, yellow needles or in tufts of canary-yellow prisms, showing slight pleochroism, m. p. 181—182° (impure), and with ferric chloride gives a yellowish-brown coloration changing to intense violet.

p-*Hydroxyphenylmaleimide*, $\begin{array}{l}CH{\cdot}C({:}N{\cdot}C_6H_4{\cdot}OH) \\ \| \\ CH\text{———————}CO\end{array}\!\!>\!O$, obtained by heating *p*-hydroxyphenylmaleinamic acid with acetyl chloride in acetone solution, separates in tufts or rosettes of acicular crystals, m. p. 154—155°.

p-*Methoxyphenylmaleimide*, $C_{11}H_9O_3N$, forms colourless, tubular crystals or small needles, m. p. 145—146°.

p-*Ethoxyphenylmaleimide*, $C_{12}H_{11}O_3N$, forms colourless, tubular crystals or silky needles, m. p. 127°, gives the normal molecular weight in freezing acetic acid, and, on reduction with sodium amalgam, yields *p*-ethoxyphenylsuccinamic acid and its imide (compare Abstr., 1896, i, 223). With aqueous or alcoholic sodium hydroxide it yields *p*-ethoxyphenylmaleinamic acid, whilst concentrated hydrochloric acid resolves it into *p*-aminophenol and fumaric acid. When treated with sodium ethoxide it gives the reddish-violet *compound*, $C_{14}H_{16}O_4NNa$, which, with sulphuric acid, yields the *compound*, $C_{14}H_{17}O_4N$, as a reddish-brown powder.

s-p-*Methoxyphenylmaleimide*, $\begin{array}{l}CH{\cdot}CO \\ \| \\ CH{\cdot}CO\end{array}\!\!>\!N{\cdot}C_6H_4{\cdot}OMe$, prepared by the action of phosphoric oxide on *p*-methoxyphenylmaleinamic acid, forms slender, yellow needles, m. p. 148·5°, and exhibits normal cryoscopic behaviour in acetic acid.

s-p-*Ethoxyphenylmaleimide*, $C_{12}H_{11}O_3N$, obtained from the corresponding amic acid by sublimation or by the action of phosphoric oxide, forms yellow needles, m. p. 134—135°, and has the normal molecular weight in freezing acetic acid.

p-*Hydroxyphenylfumaric diamide*,

$$OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH,$$

exists in two modifications: (1) white, decomp. at 220°, obtained by heating the acid fumarate of *p*-aminophenol at 200° in a current of carbon dioxide, and (2) yellow, which is obtained by crystallising the white variety from acetic acid, and is identical in properties with the white form.

p-*Methoxyphenylfumaric diamide*, $C_{18}H_{18}O_4N_2$, forms thin, white,

silky plates, m. p. 216°, and a yellow, apparently amorphous powder, having corresponding properties.

p-*Ethoxyphenylfumaric diamide*, $C_{20}H_{22}O_4N_2$, forms microscopic, colourless needles, m. p. 223°, and yellow, irregular plates, exhibiting marked pleochroism. T. H. P.

$\Delta^{1:5}$-Dihydrophenol or Δ^2-*cyclo*Hexenone. ARTHUR KÖTZ and TH. GRETHE (*J. pr. chem.*, 1909, [ii], 80, 473—510).—$\Delta^{1:5}$-*cyclo*-Hexadienol cannot be prepared from aliphatic compounds, but is obtained from *cyclo*hexanone in several ways.

2-*Chloro*(or *bromo*)cyclo*hexanone* is obtained by passing chlorine (or carbon dioxide charged with bromine vapour) into a mixture of *cyclo*hexanone, calcium carbonate, and water at 25—30°; the chloro-derivative has m. p. 23°, b. p. 82°/13 mm., and the bromo-derivative has b. p. 89°/14 mm. $\Delta^{1:5}$-*cyclo*Hexadienol is obtained from these compounds directly by heating with sodium acetate and glacial acetic acid or with ethereal aniline (best method), or indirectly by hydrolysing them by concentrated aqueous potassium hydroxide, the resulting cyclo*hexanon*-2-*ol*, m. p. 92—92·5°, being converted into the dihydrophenol by anhydrous oxalic acid at 100—110°, or by Tschugaeff's xanthogenic reaction.

$\Delta^{1:5}$-cyclo*Hexadienol*, b. p. 63°/14 mm., D^{18} 0·9868, n 1·4796, forms a *semicarbazone*, $C_7H_{11}ON_3$, m. p. 161°, and with 1 mol. of hydroxylamine hydrochloride an *oxime*, C_6H_9ON, m. p. 75—76°, which yields aniline by heating with acetic anhydride and then with sodium hydroxide. When the dihydrophenol is kept for eight days in a methyl-alcoholic solution of hydroxylamine (2 mols.), 3-*hydroxyamino*cyclo*hexanoneoxime*,

$$OH\cdot NH\cdot CH{<}{\begin{matrix}CH_2\cdot C(:NOH)\\ CH_2\text{——}CH_2\end{matrix}}{>}CH_2,$$

m. p. 49—51°, is obtained, which dissolves in acids and in alkalis, reduces warm Fehling's solution, and is oxidised by mercuric oxide in boiling water to cyclo*hexane*-1 : 3-*dioxime*, m. p. 155·5°, which yields cyclo*hexane*-1 : 3-*dione*, m. p. 105—106°, by hydrolysis by 10% sulphuric acid. 3-Hydroxylamino*cyclo*hexanoneoxime is reduced by sodium and boiling alcohol to 1 : 3-*diamino*cyclo*hexane*, the *platinichloride* of which, $C_6H_{10}(NH_2)_2,H_2PtCl_6$, has m. p. 256° (decomp.).

3-*Chloro*cyclo*hexanone*, b. p. 91—92°/14 mm., is obtained by passing dry hydrogen chloride into a dry ethereal solution of $\Delta^{1:5}$-*cyclo*-hexadienol. The dihydrophenol absorbs bromine, forming a dibromo-additive compound, which yields phenol by loss of 2 mols. of hydrogen bromide. The dihydrophenol also yields a *benzylidene* compound, $CHPh:C{<}{\begin{matrix}CH_2\cdot CH_2\\ CO\text{—}CH\end{matrix}}{\gg}CH$, b. p. 172—175°/15 mm., by treatment with benzaldehyde and cold alcoholic sodium ethoxide.

The action of carbon dioxide on an ethereal solution of $\Delta^{1:5}$-*cyclo*-hexadienol in the presence of sodium leads to the formation of Δ^3-cyclo*hexene*-2-*one*-1-*carboxylic acid* ($\Delta^{1:3}$-*dihydrosalicylic acid*), the *ethyl* ester of which, prepared from the silver salt, has b. p. 115—117°/15 mm. The constitution of the acid is proved as follows.

In the presence of sodium ethoxide, $\Delta^{1:5}$-*cyclo*hexadienol condenses with ethyl oxalate to form the *ethyl* ester,

$$CO_2Et\cdot CO\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO-CH\end{matrix}>CH,$$

which gives a red coloration with ferric chloride, and loses carbonic oxide by distillation in a vacuum, yielding ethyl $\Delta^{1:3}$-dihydrosalicylate, b. p. 115°/14 mm. (blue colour with ferric chloride), identical with the preceding ester. Since by treatment with potassium and methyl iodide in xylene the ester yields the *methyl* homologue,

$$CO_2Et\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CO-CH\end{matrix}>CH,$$

b. p. 110—125°/12 mm., which can be converted into 2-methyl*cyclo*hexanone, it must have the constitution assigned to it, and not that of Δ^6-cyclo*hexen-2-one-*1-*carboxylic acid,* m. p. 128°, which could not form a methyl derivative under the preceding conditions. This acid is obtained by heating ethyl 1-bromo*cyclo*hexan-2-one-1-carboxylate with sodium acetate and acetic acid, or the corresponding bromo-compound with ethereal aniline, and hydrolysing the *ethyl* Δ^6-cyclo*hexen-2-one-*1-*carboxylate,* b. p. 103°/12 mm., produced. It yields $\Delta^{1:5}$-*cyclo*hexadienol by distillation with soda-lime.

When an ethereal solution of *cyclo*hexanone is gently boiled with sodamide and the resulting sodium derivative treated with carbon dioxide, cyclo*hexan-2-one-*1-*carboxylic acid* is obtained ultimately; the *barium* and *silver* salts are mentioned, and the *ethyl* ester has b. p. 108—109°/12 mm.

Ethyl 4-methyl*cyclo*hexan-2-one-1-carboxylate yields ethyl 1-bromo-4-methyl*cyclo*hexan-2-one-1-carboxylate by bromination, which is boiled with ethereal aniline, whereby *ethyl* 4-*methyl*-Δ^6-cyclo*hexen-2-one-*1-*carboxylate,* b. p. 113°/12 mm., is produced; the corresponding *acid* has m. p. 153°, and by distillation with soda-lime yields 5-*methyl*-Δ^2-cyclo*hexenone,* b. p. 189°, which forms a *semicarbazone,* m. p. 158°.

C. S.

Synthesis of Octa-, Deca-, and Dodeca-methylene Compounds of the Aliphatic Series. JULIUS VON BRAUN [and A. TRÜMPLER] (*Ber.*, 1909, **43**, 4541—4554).—On coupling two molecules of phenyl δ-iodobutyl ether by means of sodium, αθ-diphenoxyoctane is obtained in good yield, and the yield is increased when the same process is applied to the phenyl ethers of iodoamyl or iodohexyl to form diphenoxy-decane and -dodecane derivatives. The further the iodine is distant from the phenoxy-group the more the compound tends to behave as a simple non-substituted alkyl iodide.

The replacement of the phenoxy-group by iodine, effected by heating with hydriodic acid in sealed tubes, becomes more difficult the larger the distance between the phenoxy-groups. Whereas diphenoxypentane only requires heating at 120° with 2 c.c. of fuming hydriodic acid per gram of ether, both diphenoxyhexane and diphenoxyoctane require heating at 130—135° with 3 c.c. of the acid; diphenoxydecane must be heated at 150° with 4 c.c. of the halogen acid, and to convert diphenoxydodecane, it is necessary to heat with a large excess of

hydriodic acid at 175—180°. This method of preparing di-iodo-paraffins is not available much higher in the series.

Phenyl δ-iodobutyl ether is condensed in presence of sodium to αθ-diphenoxyoctane, $OPh\cdot[CH_2]_8\cdot OPh$ (compare Solonina, Abstr., 1899, i, 681), m. p. 80°, which, when heated with hydrogen iodide at 135°, forms *αθ di-iodo-octane*, $I\cdot[CH_2]_8\cdot I$, b. p. 179—180°/13 mm.

αθ-Diphenylthioloctane, $C_8H_{16}(SPh)_2$, prepared by the interaction of di-iodo-octane, sodium, and thiophenol, is a colourless, crystalline solid, m. p. 83°.

αθ-Dianilino-octane, $C_6H_{16}(NHPh)_2$, is formed quantitatively by the interaction of the iodide with aniline. It has m. p. 61—62°; the *picrate* and *nitroso*-derivative are oily; the *benzoyl* derivative has m. p. 110—112°.

The condensation of phenyl ε-iodoamyl ether by sodium gives rise to compounds which may be separated by steam distillation into a volatile and a non-volatile product. The former, b. p. 117—120°/15 mm., consists of a mixture of phenyl-*n*-amyl ether and phenylamylenyl ether, $CH_2:CH\cdot[CH_2]_3\cdot OPh$; when the mixture is heated with hydrogen iodide, *n*-amyl iodide, b. p. 62°/20 mm., and 1 : 4-di-iodopentane, b. p. 140°/20 mm., are obtained, the structure of the latter being proved by condensation with aniline to be phenyl-2-methylpyrrolidine (Scholtz and Friemehlt, Abstr., 1899, i, 541), b. p. 136—138°/16 mm.; picrate, m. p. 108—109°; platinichloride, m. p. 135°.

Amyl iodide, on prolonged heating with potassium cyanide, forms *hexonitrile*, a colourless liquid of penetrating, but not unpleasant, odour, b. p. 160°.

The non-volatile portion, *ακ-diphenoxydecane*, has m. p. 85°; it yields *ακ-di-iododecane*, $C_{10}H_{20}I_2$, a faintly-coloured oil, b. p. 212—215°/16 mm., which crystallises in very stable, lustrous, glass-like crystals, m. p. 29—30°. The corresponding *ακ-diphenylthioldecane* has m. p. 85°.

Decane-ακ-dicarboxylic acid, m. p. 125°, is identical with an acid described by Nordlinger (Abstr., 1890, 1237). The *nitrile*, prepared by heating di-iododecane with potassium cyanide, is a colourless, almost odourless liquid, m. p. 225—228°/17 mm., which solidifies when cooled with ice.

Di-iododecane, when heated with potassium phthalimide at 180—190°, forms a *phthalimide*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot[CH_2]_{10}\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

m. p. 136°. The corresponding *phthalamic acid*,

$$C_{10}H_{20}(NH\cdot CO\cdot C_6H_4\cdot CO_2H)_2,$$

separates in well-formed, colourless crystals, m. p. 129°. When the phthalimide is heated for four hours at 180° with hydrogen chloride, ακ-diaminodecane, m. p. 60°, is formed. The dibenzoyl derivative has m. p. 152°.

Phenyliodohexyl ether is condensed by sodium to volatile products and *αμ-diphenoxydodecane*. It is converted with difficulty into αμ-di-iodododecane, m. p. 41°.

When decane-ακ-dicarboxylnitrile is reduced, the *hydrochloride* of *αμ-diaminododecamethane* is formed; this does not melt at 250°; the

platinichloride, decomp. 225°. The free diamine is a colourless solid, m. p. 66—67°; the *benzoyl* derivative has m. p. 153°, and the benzenesulphonyl compound crystallises in nacreous plates, m. p. 99°.

E. F. A.

Monohalogenated Phenols. WILLIAM J. WOHLLEBEN (*Ber.*, 1909, **42**, 4369—4375).—Commercial *o*-chlorophenol contains phenol, as it yields phenyl benzoate, m. p. 70°, on benzoylation. To purify it, it is conveniently shaken with an excess of potassium carbonate and the phenol present extracted with ether. o-*Chlorophenyl acetate* is a clear, colourless oil, b. p. 103°/15 mm., m. p. $-20\cdot5°$ to $-19\cdot5°$, D_4^{20} 1·2166. o'-*Chlorophenyl* m-*nitrobenzoate* crystallises in characteristic bunches of prisms, m. p. 98°.

m-*Chlorophenyl acetate* is an oil, b. p. 116·5°/21 mm., D_4^{20} 1·2209; it crystallises in needles, m. p. $-1\cdot5°$ to 0·5°; the *benzoate* crystallises in glistening prisms, m. p. 71—72°; the m-*nitrobenzoate* separates in colourless, matted needles, m. p. 94—95°. *m*-Chlorophenetole (compare Guttermann, *Annalen*, 1907, **357**, 349) is a clear oil with a pleasant odour; b. p. 204—205°/717 mm., D_4^{20} 1·1712. o-*Chloro*-p-*hydroxyazobenzene*, $NPh\colon N\cdot C_6H_3Cl\cdot OH$, crystallises in glistening, orange-red needles, m. p. 114—115°.

p-*Chlorophenyl acetate* is an oil, b. p. 108°/12·5 mm., D_4^{20} 1·2248; it forms long, crystal needles, m. p. 7—8°. All three chlorophenols dissolve when shaken with concentrated sodium carbonate, and are precipitated by carbon dioxide. p'-*Chlorophenol* m-*nitrobenzoate* forms lustrous, silky, concentrically grouped needles, m. p. 124·5°.

o-*Bromophenyl acetate* is a clear oil with an ethereal odour, b. p. 149—150°, D_4^{20} 1·4924.

m-*Bromophenyl acetate* has b. p. 149°/40 mm., D_4^{20} 1·5478. It does not mix with benzene; the *benzoate* crystallises in colourless, microscopic prisms or rhombic plates, m. p. 86°.

p-*Bromophenyl acetate* is an oil of unpleasant odour, b. p. 128°/35 mm., which forms colourless needles, m. p. 21·5°; the benzoate, which has been variously described, crystallises from alcohol in colourless, rhombic plates, m. p. 104°.

p-*Iodophenyl acetate* forms colourless plates, m. p. 32—32·5°; the *benzoate* crystallises in colourless, six-sided or rhombic plates, or in matted needles, m. p. 118·5°—119·5°; the m-*nitrobenzoate* separates in lustrous, long, colourless needles, m. p. 120—121°; the *benzenesulphonate* crystallises in long, colourless plates, or in bunches of lustrous, matted needles, m. p. 52—53°.

E. F. A.

Preparation of Aromatic Nitrohydroxy-compounds. RICHARD WOLFFENSTEIN and OSKAR BOETERS (D.R.-P. 214045. Compare Abstr., 1908, i, 629).—It has been shown previously that the action of nitric acid on aromatic hydrocarbons in the presence of mercury results in the formation of nitrohydroxylated products; it is now found that nitrous acid or the oxides of nitrogen react in a similar manner. The treatment of benzene with nitrogen peroxide in the presence of mercury yields 2 : 4-dinitrophenol, whilst with fuming nitric acid at a high temperature picric acid is obtained.

F. M. G. M.

Preparation of Arylalkyl-*p*-aminophenols. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 213592. Compare Abstr., 1909, i, 914).—The following compounds prepared by the reduction (with zinc in alkaline solution) of the condensation products from substituted *p*-aminophenols and aromatic aldehydes are employed for photographic purposes.

3-*Chloro*-4-*benzylideneaminophenol*, m. p. 180—181°, from the condensation of benzaldehyde with 3-chloro-4-aminophenyl sulphate, yields, on reduction, 3-*chloro*-4-*benzylaminophenol*, which was not obtained in crystalline form; its crystalline *hydrochloride* has m. p. 195° (decomp.).

4-*Benzylideneamino*-m-*cresol*, m. p. 133°, prepared from 4-amino-*m*-tolyl sulphate and benzaldehyde, yields, by reduction, 4-*benzylamino*-m-*cresol*, which separates in the form of its sparingly soluble *sodium* salt; the *hydrochloride* has m. p. 220° (decomp.), and from this, on treatment with sodium sulphide, the free base, m. p. 84°, is obtained.

F. M. G. M.

Estimation of Ortho- and Para-Sulpho-groups in Phenolsulphonic Acids. JULIUS OBERMILLER (*Ber.*, 1909, 42, 4361—4369). —It is well known that by treatment with bromine, phenolsulphonic acids lose their *o*- and *p*-sulphonic groups, which are eliminated as sulphuric acid. The latter can be estimated gravimetrically, but to avoid too high results the following directions must be closely followed.

The bromine solution consists of water containing 1 per cent. of sodium bromate (or 1·1% of potassium bromate) and 5% of potassium bromide; it contains 3·1—3·2% of potential bromine. The phenolsulphonate, 0·2 to 0·3 gram, with three times the weight of barium chloride, and 10 c.c. of hydrochloric acid, D 1·19, are diluted to 100 c.c. with water. The solution is heated to 60—65°, and slowly treated, with certain precautions, with the bromine solution until a faint persistent, yellow colour is produced. A little alcoholic phenol is added to absorb the excess of bromine, and then sufficient alcohol to dissolve the tribromophenol. The liquid is boiled and decanted while warm from the barium sulphate, which is repeatedly washed in the beaker with 50% alcohol and then with hot water. The barium sulphate is finely filtered and weighed in the usual way. Barium *o*-phenolsulphonate, magnesium *p*-phenolsulphonate, and barium phenol-2:4-disulphonate (Abstr., 1907, i, 910) have been satisfactorily treated by this process, although the results are still a little high. Sulpho-groups in the para-position are eliminated with greater difficulty than those in the ortho-position. Of the salts of doubtful constitution, previously obtained by the fractional crystallisation of the salts prepared from the sulphonation products of phenol (*loc. cit.*), the "aluminium salt of the para-acid" proves to be the magnesium salt, the "magnesium salt of the ortho-acid" to be the magnesium salt of the para-acid, the "barium salt of the ortho-acid" to be barium chloride, and the "magnesium salt of the disulphonic acid" to be a mixture of calcium phenol-2 : 4-disulphonate and magnesium *o*-phenolsulphonate.

C. S.

Abnormal Reduction of an Aromatic Nitro-compound with Tin and Hydrochloric Acid and an Interesting Case of Dimorphism. OTTO DE VRIES (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 305—306; *Rec. trav. chim.*, 1909, **28**, 395—407).—3-Nitro-4-methoxytoluene, when reduced with iron and acetic acid, yields the corresponding amine, whilst treatment with tin and hydrochloric acid leads to the formation of 6-*chloro-3-amino*-p-*tolyl methyl ether*, which forms colourless needles, m. p. 106° (corr.); the *acetyl* derivative has m. p. 115° (corr.). In order to arrive at the constitution of the compound, it was converted into 3 : 6-*dichloro*-p-*tolyl methyl ether*, which was obtained in a labile modification, crystallising in needles, m. p. 29°, and a stable modification, forming flat crystals, m. p. 44°. The fused substance, when cooled, yields the labile variety, which, by inoculation or in an infected region, passes spontaneously into the stable form.

W. H. G.

2 : 5-Diphenylphenol. FRITZ FICHTER and OTTO WALTER (*Ber.*, 1909, **42**, 4311—4313).—2 : 5-Diphenylphenol (Abstr., 1903, i, 481) yields 2 : 5-*diphenylphenyl* p-*toluenesulphonate*, $C_{25}H_{20}O_3S$, m. p. 102°, by boiling with alcoholic potassium hydroxide, and *p*-toluenesulphonyl chloride. p-*Nitrobenzeneazodiphenylphenol*, $OH\cdot C_6H_2Ph_2\cdot N_2\cdot C_6H_4\cdot NO_2$, red needles, decomposing at 243—245°, is obtained by the action of diazotised *p*-nitroaniline on alcoholic diphenylphenol in alkaline solution.

The attempt to produce a benzene ring by the condensation of styrylitaconic acid (Abstr., 1901, i, 594) by acetic anhydride at 130° resulted in the formation of the *anhydride*,

$$\begin{matrix}O\text{——}CO\\ |\qquad\quad\\ CO\cdot CH_2\end{matrix}\!\!>C{:}CH\cdot CH{:}CHPh,$$

m. p. 180°.

The nitration of phenylsuccinic acid by nitric acid, D 1·52, at 0° results in the formation of *o-nitrophenylsuccinic acid*, m. p. 188°, and p-*nitrophenylsuccinic acid*, m. p. 218°—220° (decomp.); p-*acetylaminophenylsuccinic acid* has m. p. 218°.

The reduction of *o*-nitrophenylsuccinic acid by ammoniacal ferrous sulphate yields *dihydrocarbostyril-γ-carboxylic acid*,

$$C_6H_4<\begin{matrix}CH(CO_2H)\cdot CH_2\\ NH\text{————}CO\end{matrix},$$

m. p. 223°, which separates from water in colourless needles. C. S.

The Fluorene Series. I. JULIUS SCHMIDT and HERMANN STÜTZEL (*Annalen*, 1909, **370**, 1—40. Compare Abstr., 1908, i, 415; Schmidt and Mezger, Abstr., 1907, i, 43; Schmidt and Söll, *ibid.*, 1054).—Although fluorenoneoxime is converted by zinc and acetic acid into 9-aminofluorene, when it is reduced by tin and hot concentrated hydrochloric acid it yields fluorenyl ether, the formation of which may be explained thus: $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C{:}NOH \longrightarrow \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CO \longrightarrow \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH\cdot OH \longrightarrow \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH\cdot O\cdot CH<\!\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$. The most remarkable property of this substance is its red colour, which cannot be due to a

quinonoid structure, for fluorene and 9-hydroxyfluorene are quite colourless, but is probably the result of an accumulation of benzene nuclei.

It is shown that the known 9-hydroxyfluorene is directly connected with α-9-aminofluorene, since it yields α-9-acetoxyfluorene when heated with acetic anhydride; attempts to prepare the 9-hydroxyfluorene, corresponding with β-9-aminofluorene, were unsuccessful.

When 9-acetylaminofluorene is warmed with nitric acid, it yields 1 : 8-dinitrofluorenone, many derivatives of which have been prepared. The behaviour of 1 : 8-dinitrofluorenone towards stannous chloride and hydrochloric acid is remarkable, in that a nitro-group is eliminated with the formation of 1-amino-9-hydroxyfluorene, a compound not without interest, for it is red, and the substances derived from it are also intensely coloured. When 1 : 8-dinitrofluorenoneoxime is reduced with tin and hydrochloric acid, it likewise yields 1-amino-9-hydroxyfluorene, but when treated with zinc dust and acetic acid it is converted into 1 : 9-diaminofluorene.

Fluorenyl ether crystallises in red prisms, m. p. 254—255°, and when warmed with concentrated nitric acid yields a yellow *substance*, m. p. about 285°.

α-9-Hydroxyfluorene, m. p. 153°, is obtained by the action of nitrous acid on either α- or β-9-aminofluorene, possibly because β-9-hydroxyfluorene is labile and passes into the stable α-form; the *benzoate*, $C_{20}H_{14}O_2$, crystallises in colourless leaflets, m. p. 161°.

When 9-aminofluorene is reduced with amyl alcohol and sodium, it yields an oily *substance*, which is either 9-aminodihydrofluorene or 9-aminotetrahydrofluorene; the *picrolonate* forms yellow crystals, m. p. 218°; attempts to reduce 9-aminofluorene with hydrogen in the presence of platinum-black were unsuccessful.

1 : 8-*Dinitrofluorenone*, $\begin{array}{l} CH\cdot C(NO_2)\colon C\cdot CO\cdot C\colon C(NO_2)\cdot CH \\ \vert\vert \qquad\qquad\quad \vert \qquad\quad\; \vert \qquad\qquad\quad \vert\vert \\ CH{-}{-}CH{=}C{-}{-}{-}{-}C{=}{=}CH{-}CH \end{array}$, crystallises in glistening, yellow prisms, m. p. 196—197°, and is oxidised by potassium permanganate, yielding *o*-nitrobenzoic acid; the *phenylhydrazone*, $C_{19}H_{12}O_4N_4$, forms scarlet needles, m. p. 206—207°; the *semicarbazone*, $C_{14}H_9O_5N_5$, is a brownish-yellow powder, which does not melt at 300°.

1 : 8-*Dinitrofluorenoneoxime*, $C_{13}H_7O_5N_3$, crystallises in pale yellow nodules, m. p. 250°; the *benzoyl* derivative, $C_{20}H_{11}O_6N_3$, forms pale yellow needles, m. p. 218—220°; the *acetyl* derivative, $C_{15}H_9O_6N_3$, crystallises in brownish-yellow needles, m. p. 178°; the *methyl ether*, $C_{14}H_9O_5N_3$, forms small, pale yellow, crystalline nodules, m. p. about 150° (decomp.).

1-*Amino-9-hydroxyfluorene*, $C_{13}H_{11}ON$, crystallises in dark red needles, m. p. 142°; the *acetyl* derivative, $C_{15}H_{13}O_2N$, forms small, brownish-yellow crystals, m. p. 200°; the *benzoyl* derivative,

$$C_{20}H_{15}O_2N,$$

crystallises in flesh-coloured needles, m. p. 260°; the position of the acyl group in the compounds just described is not known; the *hydrochloride*, $C_{13}H_{11}ON,HCl$, forms small, brownish-yellow crystals, m. p. 290° (decomp.); the *nitrate* forms small, brown crystals, and

does not melt at 300°; the *picrolonate*, $C_{23}H_{19}O_6N_5$, forms greenish-yellow crystals, m. p. 246° (decomp.); the *additive* product with phenylcarbimide, $C_{27}H_{21}O_3N_3$, forms small, red crystals, m. p. 262°. The *diazo*-derivatives couples with phenols and amines, yielding *azo*-dyes, and when boiled with water yield 1 : 9-*dihydroxyfluorene*, a reddish-brown, crystalline substance, m. p. 218—220°; the *diacetate* crystallises in reddish-brown needles, and does not melt at 300°.

1 : 9-*Diaminofluorene*, $C_{13}H_{12}N_2$, forms small, white crystals, m. p. about 120°; the *diacetyl* derivative, $C_{17}H_{16}O_2N_2$, crystallises in white leaflets, m. p. 293°; the *dibenzoyl* derivative, $C_{27}H_{20}O_2N_2$, forms small, white needles, m. p. about 310°; the *picrate* crystallises in greenish-yellow leaflets, m. p. 205° (decomp.); the *picrolonate*, $C_{23}H_{20}O_5N_6$, forms yellowish-brown crystals, and decomposes at about 235°; 1 : 9-*diphenylcarbamidofluorene*, prepared from the diamine and phenylcarbimide, forms small, white crystals, m. p. 258—260°.

W. H. G.

Cholesterol. I. The Xanthogen Reaction. LEO TSCHUGAEFF and A. GASTEFF (*Ber.*, 1909, **42**, 4631—4634).—The authors have applied the xanthogen reaction (Abstr., 1900, i, 129; 1905, i, 71) to cholesterol. In order to avoid molecular rearrangement in the formation of potassium cholesteroxide, the compound was prepared by the action of a toluene solution of cholesterol on potassium amyloxide.

Methyl cholesterylxanthate, $C_{27}H_{45}\cdot O\cdot CS\cdot SMe$, is prepared by adding an excess of carbon disulphide to potassium cholesteroxide, and then warming with methyl iodide or sulphate. It crystallises in colourless needles, m. p. 126°, and has $[\alpha]_D$ −39° in 9% toluene solution. When heated, it begins to decompose at 200°, yielding methyl hydrosulphide, carbonyl sulphide, and a hydrocarbon, *cholesterylene*, $C_{27}H_{44}$. This forms colourless needles, m. p. 77°, and has $[\alpha]_D$ −107° in 11% toluene solution. It decolorises bromine, and gives the usual cholesterol reactions.

J. J. S.

Preparation of Cholesteryl α-Bromo*iso*valerate. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 214157).—*Cholesteryl α-bromo*iso*valerate*, m. p. 132—133°, results from the action of α-bromo*iso*valeryl chloride on a mixture of cholesterol and diethylaniline in dry benzene; it is insoluble in water, and has no taste. The ester is hydrolysed by aqueous alkalis; these properties render it a valuable therapeutic agent.

F. M. G. M.

Phytosterols in the Family of Synantherea. Faradiol, a New Dihydric Alcohol from Coltsfoot. TIMOTHÉE KLOBB (*Compt. rend.*, 1909, **149**, 999—1001. Compare Abstr., 1903, i, 165; 1904, i, 410; 1905, i, 594).—The following substances have been isolated from the flowers of *Tussilago farfara*: (1) a saturated hydrocarbon, m. p. about 57°; (2) a *phytosterol*, having m. p. about 127°, and forming an *acetate*, m. p. 117—119°, $[\alpha]_D$ −36·7° in chloroform; (3) a viscous, yellow substance; (4) a dihydric alcohol, *faradiol*, $C_{30}H_{50}O_2$ (or $C_{31}H_{52}O_2$ or $C_{29}H_{46}O_2$). This crystallises from alcohol in large,

efflorescent, ortho-rhombic prisms, containing 1 mol. of alcohol and having m. p. 209—211°; after removal of alcohol, m. p. about 238°; $[\alpha]_D$ +45·1° in acetone. It gives Liebermann's reaction, developing a strawberry-red coloration with a green fluorescence. The *acetate* has m. p. 140—145°, $[\alpha]_D$ +63·6°, and appears to exist in two modifications; the *propionate* crystallises in pearly lamellæ, m. p. 155—158°, $[\alpha]_D$ +62·3° in benzene. The *phenylurethane*, $C_{44}H_{60}O_4N_2$, crystallises in prisms, and becomes pasty at 190—205°. W. O. W.

Dehydration of *cyclo*Hexanolpropan-β-ol. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1909, **149**, 862—864. Compare Abstr., 1909, i, 796).—When *cyclo*hexanolpropan-β-ol is heated with sulphuric acid (20%), a *hydrocarbon*, C_9H_{14}, is produced (together with a mixture of polymerides), and a *pinacoline*, $C_9H_{16}O$. The hydrocarbon is a very mobile liquid, b. p. 76°/19 mm. which combines with bromine and forms a *hydrochloride*, b. p. 96—98°/20 mm., and a *dihydrochloride*, b. p. 122—123°/18 mm. The ketone is separated by submitting the mixture to Crismer's method of oximation, when two isomeric compounds are obtained and separated by crystallisation from absolute alcohol; the *α-oxime* has m. p. 83°, the *β-oxime*, m. p. 45°; when these are treated with phenylcarbimide, they form two *carbanilino-oximes*; the α-derivative occurs in silky needles, m. p. 79—80°, the β-derivative forms hard crystals, m. p. 94—95°.

When regenerated from the mixed oximes, the ketone is obtained as a liquid, b. p. 83°/18 mm., having a camphoraceous odour; the *α-semicarbazone* forms needles, m. p. 158°, whilst the *β-semicarbazone* has m. p. 176°.

When the dehydration is effected by anhydrous oxalic acid, the same products are formed, but in different proportions. W. O. W.

New Method of Preparation of Tricyclenecarboxylic Acid (Dehydrocamphenylic Acid). JULIUS BREDT and R. MAY (*Chem. Zeit.*, 1909, **33**, 1265).—A 70—80% yield of tricyclenecarboxylic acid is obtained as follows: 50 grams of camphenilic nitrite (compare Jagelki, Abstr., 1899, i, 627) are added in small portions to 250 c.c. of concentrated sulphuric acid at 0°, the resulting product is poured on to 750 grams of ice, and the liquid submitted to steam distillation. The formation of the acid is accompanied by that of two *lactones*, m. p. 137° and 198°. W. H. G.

Preparation of *n*-Propyl *p*-Aminobenzoates. FRANZ FRITZSCHE & Co. (D.R.-P. 213459).—The anæsthetic action of the alkyl *m*- and *p*-aminobenzoates is increased by replacing methyl and ethyl with propyl as the ester-forming alkyl group. Further increase in anæsthetic action is not, however, observed when higher alkyl, hydroaromatic, or aromatic groups are employed, but rather an increase in toxicity.

n-Propyl p-*aminobenzoate* is prepared by condensing *n*-propyl alcohol and *p*-nitrobenzoic acid by means of sulphuric acid, and reducing the *n-propyl* p-*nitrobenzoates* with tin and hydrochloric acid; the latter compound forms yellow, rhombic plates, and melts at 35°. The

amino-ester is also produced directly by treating *p*-aminobenzoic acid with *n*-propyl alcohol and either sulphuric acid or hydrogen chloride. It forms needles, m. p. 73—74°. F. M. G. M.

Isomerism by Anils (Schiff's Bases). WILHELM MANCHOT and J. R. FURLONG (*Ber.*, 1909, **42**, 4383—4389).—Whereas ethyl *o*-hydroxybenzylidene-*p* aminobenzoate exists in two isomeric forms (Abstr., 1909, i, 805), only one form of the corresponding methyl ester can be obtained, and the two isomerides of the free acid could not be separated.

Methyl o-*hydroxybenzylidene*-p-*aminobenzoate* forms colourless, hexagonal crystals, m. p. 145°; they become dark red when heated above 100°, but immediately assume the original faint yellow colour when cooled.

o-*Hydroxybenzylidene*-p-*aminobenzoic acid* forms a mass of yellow or orange-red needles, which consist of almost colourless, hexagonal crystals mixed with more highly-coloured needles. When allowed to crystallise from, or heated with, amyl alcohol above 100°, the crystals become red, but lose their colour on cooling. The solid when heated becomes red at 90°, orange at 160°, sealing-wax red at 220°, bluish-red at 250°; m. p. 259° to a dark red liquid, which on cooling solidifies first to a red and finally to a yellow mass.

When exposed to light it rapidly becomes orange-red, but loses the colour again in the dark. When cooled in liquid air it becomes almost colourless.

The *hydrochlorides* of both yellow and red modifications of ethyl *o*-hydroxybenzylidene-*p*-aminobenzoate, prepared by interaction with hydrogen chloride in boiling benzene solution (yellow form) or in ethereal solution at −15° (red form), are yellow, crystalline precipitates, both m. p. 175—180° and very similar. When powdered with water, however, that from the yellow form regenerates this substance, whilst that from the red product gives a red substance, which becomes yellow at 83°, m. p. 87°. The two hydrochlorides must therefore be regarded as different.

p-*Hydroxy*-m-*methoxybenzylidene*-p-*aminobenzoic acid* is an amorphous substance, m. p. 209°. When heated with water it forms a red oil solidifying to red needles, which when dried lose their crystalline character. The colour vanishes at 75—77°, and the product has m. p. 200°.

Ethyl p-*hydroxy*-m-*methoxybenzylidene*-p-*aminobenzoate* forms glistening, faint yellow plates, m. p. 149°. It gives rise to a red, crystalline substance when treated with water and a little hydrogen chloride. The *hydrochloride* has m. p. 213—217°.

The following anils are also described; in no case were two isomerides obtained:

p-*Hydroxy*-m-*methoxybenzylidene*-o-*toluidine* is colourless, m. p. 115·5°.

p-*Hydroxy*-m-*methoxybenzylidene*-p-*toluidine* crystallises in well-formed, colourless columns, m. p. 117°.

p-*Methylbenzylidene*-p-*aminobenzoic acid* forms colourless crystals, m. p. 241°.

p-iso*Propylbenzylidene*-p-*aminobenzoic acid* yields citron-yellow crystals, m. p. 245°.

3 : 4-*Methylenedihydroxybenzylidene*-p-*aminobenzoic acid* yields a bright yellow, crystalline mass, m. p. 242°.

Benzylidene-p-*aminobenzoic acid* gives colourless crystals, m. p. 193·5°.

p-*Hydroxybenzylidene*-o-*toluidine* has m. p. 169·5°.

Ethyl p-*hydroxybenzylidene*-p-*aminobenzoate* forms a bright yellow or almost colourless mass of glistening plates, m. p. 174·5°. The *methyl* ester separates in almost colourless needles, m. p. 189°.

o-*Methoxybenzylidene*-p-*aminobenzoic acid* forms faintly yellow-coloured crystals, m. p. 227°; the *ethyl* ester has m. p. 106°.

E. F. A.

Synthesis of Aromatic Amino-acids by Rearrangements. III. Alkylaminotoluic Acids. JOSEF HOUBEN, ARNOLD SCHOTTMULLER, and ROBERT FREUND (*Ber.*, 1909, **42**, 4488—4496).—By the rearrangement, under certain conditions, of phenylcarbamates containing an alkyl group united with the nitrogen into aminobenzoates (compare Abstr., 1904, i, 1014; 1909, i, 921), the authors have succeeded in extending Kolbe's hydroxybenzoic acid synthesis to the corresponding amino-compounds. In the latter case, the yield of amino-acid never exceeds about 40%, and the final reaction must be represented by the equation:

$$2NRPh\cdot MgX + CO_2 = MgX\cdot O\cdot CO\cdot C_6H_4\cdot NR\cdot MgX + NHRPh,$$

where X = halogen, according to which the maximum possible yield is 50%, which has now been nearly approached.

The reaction has been applied to methylamino- and ethylamino-*o*-toluene, both of which give *p*-carboxylic acids, but the highest yields obtained are only about 12%, owing to the sensitiveness of the amino-toluic acids or their salts to the high temperatures at which they are formed. In the syntheses effected with the alkylanilines, considerable proportions of tertiary amino-acids were often obtained, but with the alkyltoluidines, even when large amounts of dialkyltoluidine are added, only the secondary amino-acids are obtained; these can be characterised by conversion into nitroaminic acids, or where this presents complications, into the acetyl derivatives by shaking the aqueous solutions of the alkali salts with acetic anhydride.

In the preparation of the aminotoluic acids, just as with the aniline-carboxylic acids, carbamide-like compounds are always formed in large or small proportion.

A secondary aminotoluic acid is obtained also when, in place of methylamino-*o*-toluene, a mixture of *o*-toluidine and dimethylamino-*o*-toluene is employed, so that either the *o*-toluidine undergoes methylation or the dimethylamino-*o*-toluene, demethylation.

6-*Methylamino*-m-*toluic acid*, $NHMe\cdot C_6H_3Me\cdot CO_2H$, prepared by treating a mixture of *o*-toluidine and *o*-dimethylaminotoluene with magnesium and ethyl iodide in ethereal solution, and subsequently passing carbon dioxide through the liquid, forms long, white needles,

m. p. 201°. *Ditolylmethylcarbamide* (?), $C_6H_4Me\cdot NH\cdot CO\cdot NMe\cdot C_6H_4Me$, also formed in this reaction, has m. p. 238°.

6-*Methylnitrosoamino*-m-*toluic acid*, $NO\cdot NMe\cdot C_6H_3Me\cdot CO_2H$, forms yellow needles, m. p. 153°.

6-*Ethylamino*-m-*toluic acid*, $NHEt\cdot C_6H_3Me\cdot CO_2H$, prepared from *o*-ethylaminotoluene and ethyl iodide, forms white needles, m. p. 169—170°, and gives salts with both alkalis and mineral acids. The *acetyl* derivative, $NEtAc\cdot C_6H_3Me\cdot CO_2H$, has m. p. 228°. 6-*Ethylnitrosoamino*-m-*toluic acid*, $NO\cdot NEt\cdot C_6H_3Me\cdot CO_2H$, forms long, yellow needles, m. p. 135°. The *diethylditolylcarbamide* (?),

$$CO(NEt\cdot C_6H_4Me)_2,$$

formed together with 6-ethylamino-*m*-toluic acid, forms long, white needles, and carbonises on heating.

4-*Ethylamino*-m-*toluic acid*, $NHEt\cdot C_6H_3Me\cdot CO_2H$, prepared from *p*-ethylaminotoluene and ethyl iodide, crystallises in yellow leaflets, m. p. 191°. The contiguity of the ethylamino- and carboxyl groups is indicated by the intense, bluish-violet fluorescence (similar to that shown by anthranilic acid) exhibited by aqueous and alcoholic solutions of the acid; this fluorescence disappears on addition of dilute acetic acid, apparently owing to salt formation, the basicity of the ethylamino-group being possibly increased by the methyl group in the para-position. The corresponding *nitroso-acid*, m. p. 184° (impure), was obtainable only in small quantity. The ethylaminotoluic acid is accompanied by *ditolylethylcarbamide* (?),

$$C_6H_4Me\cdot NH\cdot CO\cdot NEt\cdot C_6H_4Me,$$

m. p. 283°. T. H. P.

Addition of Ethyl Phenylacetate to Unsaturated Compounds. Walther Borsche (*Ber.*, 1909, **42**, 4496—4499).—In the author's investigations on the reactivity of the methylene group in the nitro-derivatives of ethyl phenylacetate (Abstr., 1909, i, 233, 385), it was found that these compounds do not readily form additive compounds with ethylene linkings. Sodium ethoxide attacks them rapidly, with destruction of the methylene group, whilst, under the influence of piperidine at 100°, addition occurs very slowly and imperfectly. With ethyl phenylacetate itself, however, in spite of its slight reactivity compared with the nitro-derivatives, addition takes place readily with $\alpha\beta$-unsaturated ketones and carboxylic esters in presence of sodium ethoxide. If ketones containing a methylene group are employed, ring-closure with loss of alcohol occurs under the influence of the sodium ethoxide, the resulting compounds being phenyl derivatives of dihydroresorcinol.

Ethyl $\alpha\beta$-*diphenylglutarate*, $CO_2Et\cdot CHPh\cdot CHPh\cdot CH_2\cdot CO_2Et$, prepared from ethyl phenylacetate and ethyl cinnamate, forms colourless needles, m. p. 92—93°. The free *acid*, $C_{17}H_{16}O_4$, forms colourless needles, m. p. 230—231°.

The nitrile of α-phenylcinnamic acid does not form an additive compound with ethyl phenylacetate under the conditions employed.

Ethyl γ-*benzoyl*-$\alpha\beta$-*diphenylbutyrate*, $CO_2Et\cdot CHPh\cdot CHPh\cdot CH_2Bz$, prepared from ethyl phenylacetate and benzylideneacetophenone,

forms white, silky needles, m. p. 153—154°; the corresponding *acid* is obtained as a white powder, m. p. about 240°.

2-*Phenyl*-1 : 1-*dimethyl*cyclo*hexan*-3 : 5-*dione*,

$$CMe_2<\begin{matrix}CH_2\text{—}CO\\CHPh\cdot CO\end{matrix}>CH_2,$$

prepared from ethyl phenylacetate and mesityl oxide, forms colourless leaflets containing $1H_2O$, m. p. about 135° (anhydrous).

1 : 2-*Diphenyl*cyclo*hexan*-3 : 5-*dione*, $CHPh<\begin{matrix}CH_2\text{—}CO\\CHPh\cdot CO\end{matrix}>CH_2$, obtained, together with a resinous polymeride of benzylideneacetone, by the interaction of the latter and ethyl phenylacetate, forms colourless leaflets, m. p. 159—160°. T. H. P.

***allo*- and *iso*-Cinnamic Acids.** CARL LIEBERMANN and H. TRUCKSASS (*Ber.*, 1909, **42**, 4659—4674. Compare Abstr., 1909, i, 155; also Biilmann, *ibid.*, i, 155, 382).—The authors give full particulars of the precautions necessary when working with one of these acid in order to avoid inoculation with particles of one of the isomeric acids. The hands, corks, and filter-papers are washed with alcohol and ether, and all glass vessels are "sterilised" by heating for some time at 105°.

In the preparation of the *iso*-acid, m. p. 42°, by fusing the *allo*-acid at 105°, and cooling in a flask fitted with a sterile cork, it is an advantage to work with small amounts (0·5 gram) at a time, since, with larger quantities, it is more difficult to destroy all particles of the *allo*-acid, and on solidification the minute particles left cause the separation of crystals of *allo*-acid. The *iso*-acid can be crystallised from light petroleum, b. p. 30—50°, or even b. p. 60—70° if proper precautions are taken. The acid is characterised by its rhombic crystals, their elastic nature, the soapy feel of the crystals when rubbed with a pestle, and their planes of cleavage.

No trustworthy method of obtaining the *iso*-acid, m. p. 58°, without inoculation with a particle of the acid is known.

The three acids when converted into calcium salts by shaking with water and powdered marble, and then precipitated with dilute hydrochloric acid, gave the original acid. This may be due to the fact that small particles of the original acid were not transformed into the calcium salt, and when acidified served as nuclei which produced the separation of the acid in question.

The three acids were converted into aniline salts; in each case the aniline salt had the same m. p., namely, 83—84° (Erlenmeyer, sen., Abstr., 1896, i, 46). The acid was recovered from the aniline salt by the following three methods: 1. Precipitation of the hot aqueous solution of the salt with excess of hydrochloric acid, filtering and washing the precipitate, and extracting the mother liquor with ether. 2. Rubbing the dry salt with very dilute hydrochloric acid and extracting with ether. 3. Rubbing the salt with dilute alkali, removing the aniline with ether, acidifying the alkaline liquid, and extracting the acid with ether.

By the first method, all three acids gave the *iso*-acid, m. p. 58°, with

the exception of one experiment, when the *iso*-acid, m. p. 42°, was obtained. Method 2 gave varying results. Method 3 gave either *allo*-acid or *iso*-acid, m. p. 42°.

The *iso*-acid, m. p. 58°, and the *allo*-acid can be converted into the *iso*-acid, m. p. 42°, by boiling with very dilute hydrochloric acid, and cooling in a flask provided with a cotton-wool plug.

One of the best methods of transforming the *allo*-acid or *iso*-acid, m. p. 58°, into the more fusible *iso*-acid is to dissolve in excess of sodium hydroxide solution, and, after two hours, to precipitate with hydrochloric acid (D 1·1). If precautions are taken, the acid which separates is always the *iso*-acid, m. p. 42°. J. J. S.

Bromination of *o*-Nitrophenylpropiolic Acid. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1909, **43**, 4566—4568).—By the action of bromine vapour, or of an excess of bromine in benzene on *o*-nitrophenylpropiolic acid, *αβ-dibromo-*o*-nitrocinnamic acid*,

$$NO_2\cdot C_6H_4\cdot CBr⁚CBr\cdot CO_2H,$$

is formed in small quantity mixed with nitrocinnamic acid. The dibromo-acid crystallises in stellate aggregates of colourless, lustrous needles, m. p. 222° (decomp.).

Bromination in glacial acetic acid solution leads to the formation of *ααββ-tetrabromo-*o*-nitrophenylethane*, $NO_2\cdot C_6H_4\cdot CBr_2\cdot CHBr_2$, which crystallises in rectangular, glistening, yellow plates, m. p. 186°.

E. F. A.

Preparation of *o*-ω-Trichloroacetoxybenzoic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 213591. Compare Abstr., 1909, i, 798). —*o-ω-Trichloroacetoxybenzoic acid*, $CO_2H\cdot C_6H_4\cdot O\cdot CO\cdot CCl_3$, can be prepared by treating salicylic acid or its salts with trichloroacetic anhydride or trichloroacetyl chloride in the presence of a tertiary base, such as dimethylaniline. It forms colourless crystals, m. p. 150—152°. The acid chloride or anhydride can be replaced by the free acid if phosphorus trichloride or phosphoric oxide is also employed. The chlorination of *o*-acetoxybenzoic acid leads to substitution in the phenyl nucleus instead of in the side-chain.

F. M. G. M.

Preparation of Aromatic Halogenalkyloxycarboxylic Acids. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 213593).—It has been found that when the tolyl halogen alkyl ethers are oxidised with either permanganate, manganese dioxide with sulphuric acid, or dichromate and sulphuric acid they yield the corresponding carboxylic acids without any loss of halogen from the alkyloxy-group.

p-*Bromoethoxybenzoic acid*, $CO_2H\cdot C_6H_4\cdot O\cdot C_2H_4Br$, colourless, glistening leaflets, m. p. 178°, is thus prepared from *p*-tolyl bromoethyl ether; the *ethyl* ester has m. p. 76°.

o-*Bromoethoxybenzoic acid*, from *o*-tolyl bromoethyl ether, melts at 164°. F. M. G. M.

Preparation of *o*-Thymotic Acid and of Certain of its Derivatives. ROSARIO SPALLINO and G. PROVENZAL (*Gazzetta*, 1909, **39**, ii, 325—336).—By the action of sodium on a xylene solution of thymol through which a current of carbon dioxide was passed, the author has prepared *o*-thymotic acid, which forms monoclinic crystals [ROSATI, $a:b:c = 1{\cdot}0724:1:0{\cdot}9039$; $\beta = 93°24'$], m. p. 127°. Kolbe and Lautemann (*Annalen*, 1860, **115**, 205) and Kobek (Abstr., 1884, 56) gave 120°, and Puxeddu (Abstr., 1906, i, 995), 123°. The *silver* and *sodium* salts were prepared; the *methyl* ester,

$$\mathrm{CPr}{<}\begin{matrix}\mathrm{CH}\text{————————}\mathrm{CH}\\ \mathrm{C(OH){:}C(CO_2Me)}\end{matrix}{>}\mathrm{CMe},$$

b. p. 142°/18·5 mm., and the *ethyl* ester, $C_{13}H_{18}O_3$, b. p. 153°/18·5 mm., are pale yellow, oily liquids.

The action of phosphoric oxide or phosphoryl chloride on *o*-thymotic acid in xylene solution yields a mixture of two isomeric thymotides (compare Naquet, *Bull. Soc. chim.*, 1863, **4**, 96; 1865, **6**, 98). The *first*, $C_{22}H_{24}O_4$, forms colourless, rhombohedral crystals (ROSATI, $a:c = 1:1{\cdot}1092$; $\alpha = 94°11'$], m. p. 174°, and is hydrolysed readily by alcoholic potassium hydroxide, and more slowly by concentrated sulphuric acid, yielding *o*-thymotic acid; the *second* isomeride, m. p. 209°, forms biaxial crystals, and is readily hydrolysed by alcoholic potassium hydroxide or concentrated sulphuric acid. The two thymotides exhibit different solubilities in various solvents, but both give normal molecular weights in freezing benzene or phenol. They are probably stereoisomerides of the structure:

$$\begin{array}{l}\mathrm{CH{:}CMe{\cdot}C{\cdot}CO{\cdot}O{\cdot}C{\cdot}CPr{=}CH}\\ \;\,|\qquad\quad\;\;\,\|\qquad\qquad\;\|\qquad\quad\;\;|\\ \mathrm{CH{=}CPr{\cdot}C{\cdot}O{\cdot}CO{\cdot}C{\cdot}CMe{:}CH}\end{array}.$$

T. H. P.

Action of Free Hydroxylamine on Coumarin. LUIGI FRANCESCONI and GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 183—188).—The authors traverse the statement made by Posner (Abstr., 1909, i, 583) that the dihydroxylaminohydrocoumarin described by them (*ibid.*, i, 233) is a mixture of β-hydroxylamino-dihydrocoumarohydroxamoxime hydroxide and β-aminodihydro-coumaric acid (termed aminohydrocoumaric acid by the present authors).

Further experiments show that at 0° coumarin takes up 3 mols. of hydroxylamine, giving β-hydroxylaminodihydrocoumarohydroxam-oxime hydroxide, m. p. 123°. At the ordinary temperature (20—25°), that is, under the conditions in which 1 mol. of hydroxl-amine is added to the lactonic linking of santonin, only 2 mols. of hydroxylamine are added to coumarin, the resultant product being dihydroxylaminohydrocoumarin, m. p. 130—131°, which is far more stable than β-hydroxylaminodihydrocoumarohydroxamoxime hydroxide. At the b. p. of methyl alcohol, either no reaction occurs or amino-hydrocoumaric acid is formed. T. H. P.

Anhydrides of *iso*Phthalic and Terephthalic Acids. JOHN E. BUCHER and W. CLIFTON SLADE (*J. Amer. Chem. Soc.*, 1909, **31**, 1319—1321).—It has been stated in certain well known text-books that *iso*phthalic and terephthalic acids cannot form anhydrides. It

has been found, however, that the anhydrides of both acids can be obtained by dissolving the acids in acetic anhydride and distilling off the liquid at 200°. The *anhydrides* are thus obtained as granular substances, which decompose on heating without showing definite m. p., are not volatile, and are readily soluble in warm solutions of alkali hydroxides. The properties of these compounds indicate that they have a high molecular weight, and may be represented by the formula $[C_6H_4(CO)_2O]_x$. E. G.

β-Phenylglutaconic Acid. FRANZ FEIST and G. POMME (*Annalen*, 1909, **370**, 72—81. Compare this vol., i, 7).—β-Phenylglutaconic acid, prepared by any one of the known methods (compare Michael, Abstr., 1894, i, 172; Ruhemann, Trans., 1899, **75**, 248; Buchner and Schroeder, Abstr., 1902, i, 319), is obtained in one modification only, m. p. 154—155°, which is regarded by Buchner and Schroeder as the *cis*-form, because of its close relationship to the anhydride; this view, however, is shown to be incorrect; the acid, m. p. 154—155°, must have the *trans*-configuration, for the anhydride when acted on by alkali in the presence of casein yields on precipitation with silver nitrate a silver salt, which, when suspended in ether and decomposed by hydrogen sulphide, yields the anhydride, whereas, in the absence of casein, the acid, m. p. 154°, is obtained; the presence of the anticatalyst prevents the transformation of the labile *cis*-isomeride into the *trans*-acid, but the former, being unstable, passes into the anhydride. The crystalline *barium* and *calcium* salts were analysed. The *semi-anilide*, $C_{17}H_{15}O_3N$, prepared from the anhydride and aniline, forms pearly crystals, m. p. 174°; the *barium* salt,

$$(C_{17}H_{14}O_3N)_2Ba,4H_2O,$$

was analysed; the corresponding *semi*-p-*toluidide*, $C_{18}H_{17}O_3N$, forms aggregates of pearly crystals, m. p. 184°. The *anil*,

$$CPh{<}{\begin{matrix}CH-CO\\CH_2\cdot CO\end{matrix}}{>}NPh,$$

obtained by the action of aniline on the acid at 130°, crystallises in colourless needles, m. p. 232°; the corresponding p-*tolil*, $C_{18}H_{15}O_2N$, crystallises in needles, m. p. 248·5—249°.

β-Phenyl-α-benzylglutaconic acid, $CO_2H\cdot CH(CH_2Ph)\cdot CPh{:}CH\cdot CO_2H$, prepared by the action of benzyl chloride and sodium ethoxide on ethyl β-phenylglutaconate at 110° under pressure, is an oil; the *barium* and *silver* salts were analysed.

Ethyl β-phenylglutaconate, when heated with benzaldehyde and an alcoholic solution of potassium hydroxide, yields *β-phenyl-α-benzylideneglutaconic acid*, $CO_2H\cdot C({:}CHPh)\cdot CPh{:}CH_2\cdot CO_2H$, crystallising in compact needles, m. p. 210·5°.

β-Phenylglutaconic acid does not combine with hydrogen bromide, but absorbs bromine slowly, yielding *αβ-dibromo-β-phenylglutaric acid*, $CO_2H\cdot CHBr\cdot CPhBr\cdot CH_2\cdot CO_2H$, which forms crystals, m. p. 166° (decomp.). W. H. G.

Action of Sulphuric Acid on Santonin. II. GUIDO BARGELLINI and S. SILVESTRI (*Gazzetta*, 1909, **39**, ii, 346—349. Compare Abstr., 1909, i. 723).—The authors have investigated the products obtained

by the action of sulphuric acid (D 1·5) on santonin at various temperatures. At the ordinary temperature (about 20°), *l*-desmotroposantonin is formed; at 30—50°, a mixture of *l*-desmotroposantonin and desmotroposantonin, and at 50—90°, a mixture of desmotroposantonin, $[\alpha]_D$ +112°, *d*-santonous acid, and a red, tarry matter. At 100°, no desmotroposantonin is formed, the product consisting entirely of *d*-santonous acid and the red tar. Desmotroposantonin is converted into these two substances by the action of sulphuric acid (D 1·5) at 100°, and hence forms the first product of the action of the acid on santonin, its conversion into santonous acid by reduction being probably accompanied by a corresponding oxidation to a ketosantonous acid, thus: $\vdots CH\cdot OH + H_2 = H_2O + \vdots CH_2$ (santonous acid) and $\vdots CH\cdot OH + O = H_2O + \vdots CO$ (ketosantonous acid). The red, tarry matter is being investigated in order to ascertain whether it contains a ketosantonous acid.

The action of syrupy phosphoric acid (D 1·725) on santonin is similar to that of sulphuric acid (D 1·5). T. H. P.

Benzaldehydesulphoxylates. MAX BAZLEN (*Ber.*, 1909, **42**, 4634—4637. Compare Abstr., 1905, ii, 240).—In reply to Fromm and Erfurt (Abstr., 1909, i, 936), the author gives full details for the preparation of sodium benzaldehydesulphoxylate, $NaHSO_2,C_6H_5\cdot CHO$, from sodium hyposulphite, sodium hydroxide solution, and benzaldehyde. The yield is almost theoretical, and the product can be crystallised from hot water containing a little sodium hydroxide, when it forms well developed crystals. The analogous *zinc* compound, $Zn(HSO_2,C_6H_5\cdot CHO)_2,4H_2O$, can be obtained by shaking benzaldehyde with a warm solution of zinc hyposulphite. It also forms well developed crystals. These primary salts are very unstable in contact with the air. Secondary salts have also been prepared, and are more stable. *Disodium benzaldehydesulphoxylate*, $Na_2SO_2,C_6H_5\cdot CHO,2H_2O$, forms colourless needles, and can be obtained by the action of sodium hydroxide solution on the primary sodium salt. The *barium* and *zinc* salts have been prepared. J. J. S.

Preparation of *p*-Methoxysalicylaldehyde from *p*-Hydroxysalicylaldehyde. KALLE & Co. (D.R.-P. 214153).—*p*-Methoxysalicylaldehyde was only obtained in small yield from resorcinol monomethyl ether by the Tiemann reaction owing to its instability. It has now been found possible to prepare it in a stable, pure condition by methylating *p*-hydroxysalicylaldehyde with methyl sulphate or methyl halide at 70—80° in the presence of aqueous sodium carbonate. The pure product melts at 41°, not at 62—63°, and, contrary to the statements in the literature, is readily soluble in water, particularly on warming. F. M. G. M.

New Syntheses of Vanillin. ALFRED GUYOT and A. GRY (*Compt. rend.*, 1909, **149**, 928—931. Compare Abstr., 1909, i, 236, 306, 935).—An application of the general method for the preparation of aldehydes described previously (Abstr., 1909, i, 935) to the synthesis of vanillin. The following compounds are prepared by the

condensation of mesoxalic esters or of $\alpha\beta$-diketonic esters with guaiacol.

Methyl p-*hydroxy*-m-*methoxyphenyltartronate*,

$$OMe\cdot C_6H_3(OH)\cdot C(OH)(CO_2Me)_2,$$

prisms, m. p. 115°; the *ethyl* ester crystallises in long needles, m. p. 64°. *Ethyl* p-*hydroxy*-m-*methoxyphenylacetylglycollate*,

$$C_7H_7O_2\cdot CAc(OH)\cdot CO_2Et,$$

prisms, m. p. 61°. *Ethyl* p-*hydroxy*-m-*methoxyphenylbenzoylglycollate*, $C_7H_7O_2\cdot CBz(OH)\cdot CO_2Et$, prisms, m. p. 139°.

The esters are converted into vanilloylcarboxylic acid by one of the methods mentioned previously (*loc. cit.*). A quantitative yield of pure vanillin is obtained when the acid is heated at 170° with an equal weight of dimethyl-*p*-toluidine (compare Gassmann, Abstr., 1907, i, 343).

The $\alpha\beta$-diketonic esters employed in this synthesis can be replaced by the corresponding acids. The yield of vanillin, however, is diminished, thus dihydroxytartaric acid gave only 15% of the weight of guaiacol employed. W. O. W.

Organic Syntheses by Means of Sunlight. IV. Action of Paraffins and Homologues of Benzene on Ketones and Aldehydes. EMANUALE PATERNÒ and G. CHIEFFI (*Gazzetta*, 1909, **39**, ii, 415—435. Compare Abstr., 1909, i, 393, 487).—The interaction of benzophenone and pentane under the influence of sunlight results in the formation of benzopinacone and a resin, which may be a polymeride of the characteristic compound of benzophenone and amylene (*loc. cit.*).

Benzophenone and octane yield benzopinacone and a resin, which was not identified.

Benzophenone and decane (di*iso*amyl) give benzopinacone and a resinous *additive* compound, $C_{13}H_{10}O,C_{10}H_{20}$.

In general, then, aliphatic hydrocarbons are transformed by the action of benzophenone into unsaturated hydrocarbons, which yield additive compounds with the benzophenone: $3C_{13}H_{10}O + C_nH_{2n+2} = C_{26}H_{22}O_2 + C_{13}H_{10}O,C_nH_{2n}$; these additive compounds are resins, and are decomposed into their constituents on heating.

Benzaldehyde and pentane yield hydrobenzoin (?) and polymerides of benzaldehyde, similar results being obtained with benzaldehyde and octane or decane and with *p*-tolualdehyde and octane.

With certain cyclic hydrocarbons, such as *cyclo*hexane or methyl- or dimethyl-*cyclo*hexane, benzophenone yields benzopinacone and a resin which has not yet been investigated.

Benzophenone and benzene do not seem to react under the influence of sunlight. Benzophenone and toluene yield benzopinacone and an *additive* compound, $C_{20}H_{18}O$, m. p. 79—82°, probably analogous to that formed by benzophenone and benzyl alcohol (compare Hell and Wiegandt, Abstr., 1904, i, 490).

Benzophenone and ethylbenzene give: (1) benzopinacone; (2) a *compound*, m. p. 87—89°, probably $OH\cdot CPh_2\cdot CH_2\cdot CH_2Ph$, which has the normal molecular weight in freezing benzene, and, when

treated with phosphoric oxide, yields the *triphenylpropylene*,

$$CPh_2:CH\cdot CH_2Ph,$$

m. p. 87—89°; (3) a hydrocarbon, m. p. 124—125°, probably dimethyldibenzyl (compare Moritz and Wolffenstein, Abstr., 1899, i, 424).

Benzophenone and propylbenzene yield benzopinacone and a *compound*, $C_{13}H_{10}O,C_9H_{12}$ (or $C_{13}H_{10}O,C_9H_{10}$), m. p. 94—96°, which, with phosphoric oxide, gives an *anhydride*, m. p. 80—81° and not a hydrocarbon.

Benzophenone and *p*-xylene give benzopinacone and di-*p*-methyldibenzyl (compare Moritz and Wolffenstein, Abstr., 1899, i, 910).

Benzophenone and cymene yield benzopinacone, a hydrocarbon with an unsaturated chain, and a resin, now under examination.

Benzophenone and oil of turpentine give benzopinacone and a viscous oil, b. p. 280—320°, which yields benzophenone on distillation.

Benzophenone and diphenylmethane yield $\alpha\alpha\beta\beta$-tetraphenylethanol, $CHPh_2\cdot CPh_2\cdot OH$, which forms monoclinic crystals [ZAMBONINI: $a:b:c=2\cdot9673:1:3\cdot0298$; $\beta=91°50'$], m. p. 212—214°, and has the normal molecular weight in boiling alcohol or benzene; when treated with phosphoric oxide, or with phosphorus and iodine, it yields *s*-tetraphenylethane.

With benzaldehyde and toluene, dibenzyl or diphenylmethane, no reaction occurs, the benzaldehyde undergoing rapid polymerisation. Anisaldehyde and toluene yield hydroanisoin and a resin, not yet examined. With oil of turpentine and benzaldehyde, *iso*hydrobenzoin is formed. T. H. P.

2 : 4 : 6-Tribromobenzophenone. P. J. MONTAGNE (*Rec. trav. chim.*, 1909, **28**, 449—455. Compare Abstr., 1908, i, 988).—It is shown that the yellow product formed when 2 : 4 : 6-tribromobenzophenone is heated is 6 : 8-dibromofluorenone. 2 : 4 : 6-Tribromobenzophenone is reduced to 4-bromobenzhydrol when heated with sodium hydroxide in alcohol. The latter reaction to some extent negatives the suggestion of Diels and Rhodius (Abstr., 1909, i, 351), that since the carbonyl group of ketones is reduced by sodium amyloxide, but not by sodium ethoxide, some specific action must be exerted by the amyl group in the former reagent. The author finds in fact that benzophenone is readily reduced either by potassium hydroxide or sodium hydroxide in alcohol.

6 : 8-*Dibromofluorenone*, m. p. 225°, b. p. 430° (decomp.), crystallises in slender needles from alcohol; on reduction with sodium amalgam it yields fluorene alcohol, and on oxidation with sulphuric acid and mercuric sulphate, it furnishes phthalic anhydride. T. A. H.

Derivatives of Catechol. HUGO VOSWINCKEL (*Ber.*, 1909, **42**, 4651—4654. Compare Dreczgowski, *J. Russ. Phys. Chem. Ges.*, 1893, **25**, 157).—Chloroacetocatechol diacetate, $C_6H_3(OAc)_2\cdot CO\cdot CH_2Cl$, has m. p. 110°, not 95°, and 3 : 4-diacetoxyacetophenone, m. p. 87°, not 78°.

In the preparation of chloroacetocatechol a small amount of a higher condensation product, $C_2H_4[CO\cdot C_6H_3(OH)_2]_2$ or

$$C_6H_2(OH)_2<\begin{matrix}CO\cdot CH_2\\CH_2\cdot CO\end{matrix}>C_6H_2(OH)_2,$$

is obtained when phosphoryl chloride is used. It crystallises in glistening, silver, hexagonal plates, m. p. 261°. Its *tetra-acetyl* derivative, $C_{24}H_{20}O_{10}$, crystallises from nitrobenzene in rhombic plates, m. p. 253°.

3 : 4 : *a-Triacetoxyacetophenone*, $C_6H_3(OAc)_2\cdot CO\cdot CH_2\cdot OAc$, obtained by heating chloroacetocatechol (α-chloro-3 : 4-dihydroxyacetophenone) with acetic anhydride and dry potassium acetate, crystallises in plates, m. p. 94°, and when hydrolysed with alcoholic sodium hydroxide solution yields 3 : 4-*a-trihydroxyacetophenone*,

$$C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot OH,$$

which crystallises in colourless prisms, m. p. 195°. When reduced with zinc dust and glacial acetic acid, the triacetoxy-derivative yields 3 : 4-*diacetoxyphenylethyl acetate*, $C_6H_3(OAc)_2\cdot CH_2\cdot CH_2\cdot OAc$, which crystallises in colourless plates, m. p. 85°. When heated with acetic anhydride and potassium acetate, or when heated alone at 130°, the triacetoxy-derivative yields 3 : 4-*diacetoxyphenylacetaldehyde*,

$$C_6H_3(OAc)_2\cdot CH_2\cdot CHO,$$

and acetaldehyde. The former crystallises in large, thin plates, m. p. 88°, and yields a crystalline *phenylhydrazone*. J. J. S.

Relationship between the Colour and Constitution of Unsaturated Ketones and Their Salts. HANS STOBBE (*Annalen*, 1909, **370**, 93—99).—A brief account of the nature and results of the investigations described in the following papers. W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Ketones of the Dibenzylideneacetone [Distyryl Ketone] and Dibenzylidene*cyclo*pentanone Series. HANS STOBBE and RICHARD HAERTEL (*Annalen*, 1909, **370**, 99—129).—I. *Colour of Ketones of the Dibenzylideneacetone and Dibenzylidene*cyclo*pentanone Types.*—The absorption spectra of *N*/32 solutions of ketones of the types

$$CHR:CH\cdot CO\cdot CH\cdot CHR'$$

and $\begin{matrix}CH_2\cdot C(:CHR)\\ | \\CH_2\cdot C(:CHR')\end{matrix}>CO$ in chloroform have been measured, where RR' = benzylidene, 4-methoxybenzylidene, cuminylidene, 2-ethoxybenzylidene, 3 : 4-dimethoxybenzylidene, piperonylidene, cinnamylidene, or furfurylidene; R = benzylidene and R' = 4-methoxybenzylidene, or R = benzylidene and R' = piperonylidene.

The results obtained may be summarised thus : (1) The absorption band is shortest when RR' = benzylidene. (2) Each replacement of a phenyl hydrogen atom by an alkyl or alkyloxy-group is accompanied by an increase in the length of the absorption band; the influence exerted in the ortho-position is smaller than in the para-position ; the compounds in which RR' = 3 : 4-dimethoxybenzylidene and piperonylidene have the greatest absorption. (3) Stereoisomerides, such as the stereoisomeric benzylideneanisylidene*cyclo*pentanones (compare Abstr., 1909, i, 309), exhibit different absorption. (4) The colour intensity

is increased by the addition of ethylene linkings; thus, replacement of benzylidene by cinnamylidene is accompanied by a great increase in the length of the absorption band. (5) Comparison of the spectra of the corresponding acetone and *cyclo*pentanone compounds shows that the absorption bands of the latter are about $10\mu\mu$ longer than those of the former.

Di-3 : 4-*dimethoxystyryl ketone*, $[C_6H_3(OMe)_2\cdot CH{:}CH]_2CO$, prepared by the interaction of 3 : 4-dimethoxybenzaldehyde and acetone in a dilute alcoholic solution of sodium hydroxide, forms golden-yellow crystals, m. p. 84°. *Di*-2-*ethoxybenzylidene*cyclo*pentanone*, $C_{23}H_{24}O_3$, prepared in a similar manner, has m. p. 110°; the corresponding *di*-3 : 4-*dimethoxybenzylidene* compound, $C_{23}H_{24}O_5$, has m. p. 195·5°.

Benzaldehyde, piperonaldehyde, and *cyclo*pentanone interact in a dilute alcoholic solution of sodium hydroxide, yielding two stereoisomeric *benzylidenepiperonylidene*cyclo*pentanones*,

$$\begin{array}{l}CH_2\cdot C(CH\cdot C_6H_3{:}O_2{:}CH_2)\\ |\\ CH_2\text{———————}C(CHPh)\end{array}\!\!>CO,$$

obtained as lemon-yellow crystals, m. p. 176°, and deep lemon-yellow crystals, m. p. 192°, respectively.

II. *Colour of the Crystalline Chloro-, Dichloro-, and Trichloro-acetates of the Ketones.*—The colour relationship existing between the ketones is found to exist also between the salts. The acid salts are more intensely coloured than the neutral salts. The colour intensity also increases with the strength of the acid. In the following list of salts, K represents one mol. of the ketone and A one mol. of the acid.

Distyryl ketone trichloroacetate, KA, lemon-yellow, m. p. 117°; *dichloroacetate*, KA, pale yellow.

Di-4-*methoxystyryl ketone trichloroacetate*, KA, vermilion, m. p. 93°; K2A, carmine, m. p. 63°; *dichloroacetate*, KA, orange-yellow, m. p. 96°; K2A, orange-red, m. p. 92°; *chloroacetate*, K4A, orange-yellow, m. p. 45°.

Di-2-*ethoxystyryl ketone dichloroacetate*, K2A, orange-red, m. p. 33°.

Di-3 : 4-*dimethoxystyryl ketone trichloroacetate*, KA, brown, m. p. 105°; *dichloroacetate*, KA, orange-yellow, m. p. 87°.

Dipiperonylideneacetone trichloroacetate, K2A, garnet-red, m. p. 87°; *dichloroacetate*, KA, light brown, m. p. 100°.

Styryl 4-*methoxystyryl ketone trichloroacetate*, KA, orange-red, m. p. 66°; *dichloroacetate*, KA, light yellow, m. p. 48°.

Dicinnamylideneacetone trichloroacetate, K2A, black, m. p. 110°; *dichloroacetate*, K2A, very dark red, m. p. 56°; *chloroacetate*, K6A, orange-yellow, m. p. 56°.

*Dibenzylidene*cyclo*pentanone trichloroacetate*, K2A, straw-yellow, m. p. 98°; *dichloroacetate*, KA, sulphur-yellow, m. p. 110°; *chloroacetate*, sulphur-yellow, m. p. 75°.

Di-4-*methoxybenzylidene*cyclo*pentanone trichloroacetate*, K2A, garnet-red, m. p. 73°; *dichloroacetate*, KA, orange-yellow, m. p. 133°; K2A, scarlet, m. p. 85°; *chloroacetate*, K5A, orange-red, m. p. 48°.

*Dipiperonylidene*cyclo*pentanone trichloroacetate*, K4A, black, m. p. 85—90°; KA, orange, m. p. 148°.

*Benzylideneanisylidene*cyclo*pentanone*, m. p. 147°; *trichloroacetate*,

K2A, lemon-yellow, m. p. 97°; *dichloroacetate*, KA, lemon-yellow, m. p. 68°.

*Dicinnamylidene*cyclo*pentanone trichloroacetate*, K2A, black, m. p. 89°; *dichloroacetate*, KA, orange-red, m. p. 158°.

*Difurfurylidene*cyclo*pentanone trichloroacetate*, K2A, black, m. p. 82°; *dichloroacetate*, KA, orange-red, m. p. 158°.

III. *Colour and Composition of the Hydrochlorides of the Ketones at* 15° *and* −75°.—The absorption of hydrogen chloride by the solid ketone has been investigated with the following results: (1) As a rule, at 15°, 1—2 mols., and at −75°, 4—6 mols., of hydrogen chloride are absorbed; the alkyloxy-derivatives combine with a greater proportion of hydrogen chloride than the alkyl compounds; stereoisomerides combine with the same amount of hydrogen chloride. (2) The relationships between colour and constitution observed in the case of the salts with the chloroacetic acids also exist in the case of the hydrochlorides.

IV. *Absorption Spectra of Certain Salts of the Ketones dissolved in Various Acids.*—The absorption spectra of equivalent solutions of the various ketones in sulphuric, phosphoric, chloroacetic, dichloroacetic, trichloroacetic, formic, and acetic acids, and in chloroform have been measured. It is found that the colour of solutions of the same ketone becomes more intense as the strength of the acid increases; the solutions in acetic acid are of approximately the same intensity as in chloroform, indicating the presence of only traces of acetate. It is clear that the colour of the solution depends, not only on the specific colour of the salt, but also to a great extent on the degree of hydrolysis of the salt. The effect of the constitution of the ketone on the colour of the solution remains more or less constant.

V. *Relationship between Basicity of the Ketone and the Colour of Certain Salts of the Ketones.*—The basicity of the various ketones has been determined. It is found that (1) derivatives of dibenzylideneacetone and dibenzylidene*cyclo*pentanone, obtained by substituting phenyl hydrogen atoms, are more basic than the parent substances; *iso*propyl has the smallest effect; dioxymethylene (CH_2O_2:), ethoxy- (EtO·), and methoxy- (MeO·) groups increase the basicity in the order given; the basic character is also increased by substituting furyl and cinnamenyl for phenyl; (2) the basicity of a *cyclo*pentanone compound is about two-thirds of that of the corresponding acetone compound; (3) replacement of benzylidene by *p*-methoxybenzylidene and piperonylidene increases the basicity by 2·4 and 1·7 times respectively; the basicity is roughly doubled by replacing one benzylidene group by a cinnamenyl group; (4) a relationship appears to exist between the light absorption and basicity of the ketones. W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Certain Unsaturated Cyclic Ketones, Ketone Acids, and Ketone-Esters. HANS STOBBE and SIEGFRIED SEYDEL (*Annalen*, 1909, **370**, 129—141).—An investigation on the colour relationships existing between fluorenone, fluorenone-4-carboxylic acid, and ethyl fluorenone-4-carboxylate; *allo*chrysoketonecarboxylic acid and the ethyl ester; dibromoindone, phenylindoneacetic acid, and the ethyl ester.

Fluorenone is lighter in colour than the carboxylic ester, and this again lighter than the acid. The solutions of these substances in sulphuric, trichloroacetic, dichloroacetic, and chloroacetic acids are red or dark yellow, the intensity of the solution of the same substance increasing with the strength of the acid. The solutions of the three compounds in the same acid are of unequal colour-tone, and, unlike the free substances, the solution of the ketone is darker than that of the ester, and this darker than the solution of the acid. The explanation of this is, that the ketone is more basic than the ester, which is more basic than the acid.

The other ketonic substances investigated were found to give the same results; the intensity of the solution in an acid depends both on the strength of the acid and the basicity of the ketone.

Ethyl fluorenone-4-carboxylate crystallises with $2C_6H_6$ in large, sulphur-yellow prisms, m. p. 227°.

Methyl phenylindoneacetate, $C_{18}H_{14}O_3$, forms golden-yellow needles, m. p. 108·5°. W. H. G.

Ketens. XIII. Action of Diphenylketen on Carbonyl Derivatives. HERMANN STAUDINGER [and, in part, with J. BUCHWITZ] (*Ber.*, 1909, **42**, 4249—4262. Compare Abstr., 1908, i, 246, 318, 410, 411, 602).—Experiments have been made by heating diphenylketen in the form of its solid quinoline derivative with equivalent quantities of various ketones at 130° for 1·5 hours, and determining the velocity of reaction by the amount of carbon dioxide eliminated. The reaction proceeds in two stages: the first consisting in the formation of the β-lactone: $CR_2{:}O + CPh_2{:}CO \longrightarrow \begin{array}{l} CR_2-O \\ | \qquad | \\ CPh_2\cdot CO \end{array}$, and the second in the decomposition of the lactone into carbon dioxide and an olefine derivative: $\begin{array}{l} CR_2-O \\ | \qquad | \\ CPh_2\cdot CO \end{array} \longrightarrow CO_2 + CR_2{:}CPh_2$.

It is assumed that the second reaction proceeds with an infinitely greater velocity than the first. The following results have been obtained with the ketones, the formulæ of which are given: R′·CO·CH:CHPh, 82·3; R′·CO·CN, 76·3; R′·COH, 65·9; R′·COPh, 42·5; R′·COMe, 32·8; R′·COCl, 5·5; R′·CO·O·CO·CH:CHPh, 5·3; R′·CO·OEt, 5·4; R′·CO·NPh_2, 0·0; R″·CO·CH:CH·CH:CHPh, 85·7; R″·COPh, 55·6; R″·COMe, 20·7, where R′ = ·CH:CHPh, R″ = CH:CH·CH:CHPh, and the numbers give the percentage amount of the ketone which enters into the reaction. The influence of a double linking on the reactivity of the ketone is not marked, but the results indicate that the reactivity of a ketone with diphenylketen is least when an NR_2 or OR group is attached to the carbonyl, that is, carboxylic derivatives. The carbonyl group, on the other hand, is much more reactive when attached to H, Me, or Ph, and is most reactive when unsaturated groups, for example, cyano and cinnamenyl, are present. The results are probably explicable if the state of saturation of the carbonyl group is taken into account in the different compounds.

ββ-Diphenyl-a-styrylacrylonitrile, CHPh:CH·C(CN):CPh_2, obtained

from diphenylketen-quinoline and cinnamoylformonitrile, crystallises in golden-yellow plates, m. p. 157—159°. It is not hydrolysed when boiled with acids or alkalis, but reacts with a chloroform solution of bromine, yielding the *dibromide*, $C_{23}H_{17}NBr_2$, m. p. 143—144°.

Cinnamaldehyde and diphenylketen-quinoline yield *aaδ-triphenylbutadiene*, CHPh:CH·CH:CPh$_2$, which crystallises in colourless needles, m. p. 101·5—102°. With bromine it yield a *bromo*-derivative, $C_{22}H_{17}Br$, in the form of colourless crystals, m. p. 146—148°.

Benzylideneacetophenone and diphenylketen-quinoline yield *aaβδ-tetraphenylbutadiene*, CHPh:CH·CPh:CPh$_2$, and 3-*benzoyl*-1 : 1 : 2-*triphenyl*-4-cyclo*butanone*, $COPh \cdot CH<\genfrac{}{}{0pt}{}{CHPh}{CO}>CPh_2$, which can be separated by means of ether, in which the hydrocarbon is somewhat more readily soluble. The ketone crystallises in colourless plates, m. p. 190°. It does not combine with bromine, is stable towards oxidising agents, but reacts with alkalis, yielding diphenylacetic acid. Its *dioxime* has m. p. 191—192°. The tetraphenylbutadiene crystallises in colourless, compact prisms, m. p. 146—148°. It yields a *dibromide*, $C_{28}H_{22}Br_2$, in the form of yellow crystals, m. p. 144—145°, and when oxidised in acetone solution with potassium permanganate or dichromate, yields benzaldehyde and *triphenylacraldehyde*, CPh$_2$:CPh·CHO, colourless needles, m. p. 175°.

Cinnamylideneacetophenone and diphenylketen-quinoline yield *aaβζ-tetraphenylhexa-$\Delta^{a\gamma\epsilon}$-triene*, CHPh:CH·CH:CH·CPh:CPh$_2$, and 3-*benzoyl*-1 : 1-*diphenyl*-2-*styryl*-4-cyclo*butanone*,

$$CHPh{:}CH \cdot CH<\genfrac{}{}{0pt}{}{CH(COPh)}{CPh_2}>CO.$$

The ketone crystallises in colourless needles, m. p. 120—122°, and reacts with bromine, yielding the *bromo*-derivative, $C_{31}H_{23}O_2Br$, m. p. 148—149°. The hexatriene crystallises in yellow prisms, m. p. 158—160°, and yields a *tetrabromide*, $C_{30}H_{24}Br_4$, m. p. 148—150°.

In the combination of the above compounds with bromine, one double linking always remains intact, and this is supposed to be the linking in the >C:CPh$_2$ group. Definite products could not be isolated by heating diphenylketen-quinoline with either benzylideneacetone or cinnamylideneacetone, nor yet with methyl cinnamate or cinnamodiphenylamide. J. J. S.

Phenylhydrazones of 2-Acetyl-1-naphthol [1-Hydroxy-β-naphthyl Methyl Ketone]: Alkali-insoluble Naphthols. HENRY A. TORREY and C. M. BREWSTER (*J. Amer. Chem. Soc.*, 1909, **31**, 1322—1325).—It has been shown by Torrey and Kipper (Abstr., 1908, i, 461) that the phenylhydrazones of certain hydroxyacetophenones are insoluble in aqueous alkali hydroxides, and it is stated that this insolubility is due to the combined influence of the side-chain containing the phenylhydrazine residue in the ortho-position to the hydroxyl group and of another group in the ring, such as the methoxy-group. In the present paper an account is given of the phenylhydrazones of 1-hydroxy-β-naphthyl methyl ketone and its bromo-derivative. These compounds are also insoluble in aqueous

alkali hydroxides, the insolubility in this case being due to the joint effect of the $\cdot CMe:N\cdot NHPh$ group in the ortho-position to the hydroxyl group and of the hydrocarbon residue, $\cdot CH:CH\cdot CH:CH\cdot$. The hydrazones are very stable, and can be boiled with aqueous alkali hydroxide without undergoing any change. The presence of a bromine atom in the naphthalene ring or in the phenyl group does not affect the insolubility.

4(?)-*Bromo*-1-*hydroxy*-β-*naphthyl methyl ketone*, $OH\cdot C_{10}H_5Br\cdot COMe$, m. p. 126—127°, obtained by the action of bromine on an alcoholic solution of the ketone, forms yellowish-green crystals, and condenses with benzaldehyde with production of the *benzylidene* derivative, $OH\cdot C_{10}H_5Br\cdot CO\cdot CH:CHPh$, m. p. 176—177°, which forms orange-red crystals. The *phenylhydrazone*, $OH\cdot C_{10}H_6\cdot CMe:N\cdot NHPh$, m. p. 136—137°, forms white needles. The p-*bromophenylhydrazone*, m. p. 185—186°, forms silvery-white plates, and the m-*nitrophenylhydrazone*, m. p. 232—233° (decomp.), deep red, compact needles.

The *phenylhydrazone* of the bromo-derivative crystallises in pale yellow needles, and decomposes at 159°. The p-*bromophenylhydrazone*, m. p. 160° (decomp.), forms colourless crystals, and the m-*nitrophenylhydrazone*, m. p. 201—204° (decomp.), deep, orange crystals.

E. G.

Two Isomeric *cyclo*Hexane β-Diketones. GEORGES LESER (*Compt. rend.*, 1909, **149**, 1080—1081).—When ethyl acetate is condensed with 1 : 1-dimethyl-3-*cyclo*hexanone (Abstr., 1899, i, 743), 4-*acetyl*-1 : 1-*dimethyl*-3-cyclo*hexanone*, b. p. 111—112°/13 mm., m. p. 28—29°, is formed. It yields a *semicarbazone*, m. p. 171°, has all the properties of a β-diketone, and does not react with magnesium methyl iodide.

The isomeric substance, 2-acetyl-1 : 1-dimethyl-3-*cyclo*hexanone (*loc. cit.*), is soluble in alkalis, does not form a copper derivative, and reacts with magnesium methyl iodide, forming 2-*acetyl*-1 : 1 : 3-*trimethyl*cyclo*hexan*-3-*ol*, $CH_2<\begin{matrix}CH_2 \text{———} CH_2\\ CMe(OH)\cdot CHAc\end{matrix}>CMe_2$, m. p. 88—89°, b. p. 232°/750 mm., which crystallises in prismatic needles. On boiling with 20% sulphuric acid, it furnishes the corresponding *dimethyltetrahydroacetophenone*, b. p. 207—208°/745 mm., D^{15} 0·935, n_D 1·4776, which has a strong odour of peppermint. On oxidation with permanganate, this furnishes an acid, $C_8H_{14}O_4$, m. p. 86°.

T. A. H.

Quinhydrones from Chloranil and Aromatic Hydrocarbons. HERMANN HAAKH (*Ber.*, 1909, **42**, 4594—4596. Compare Schlenk, Abstr., 1909, i, 807).—Tetrachloro-*p*-benzoquinone forms intensely-coloured *quinhydrones* with stilbene and naphthalene, which are stable at about 100°, but dissociate into their components at the ordinary temperature ; the violet *quinhydrones* derived from acenaphthene and acenaphthylene are stable at the ordinary temperature. Interesting is the fact that solutions of chloranil in benzene and xylene are faintly orange and yellowish-red respectively, indicating in the second case partial quinhydrone formation.

W. H. G.

Preparation of Halogenated Anthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 214714).—Halogenated anthraquinonesulphonic acids were formerly obtained by treating the anthraquinonesulphonic acids in concentrated or fuming sulphuric acid with halogen or halogenating substances. It has now been found that in these acids the sulphonic group is replaced by halogen when this reaction occurs in the presence of water.

A *trichloroanthraquinone* (probably 1 : 3 : 4-) is obtained by the action of potassium chlorate and hydrochloric acid on an aqueous solution of sodium 1 : 4-dichloroanthraquinone-β-sulphonate. It forms yellow needles, m. p. 237°.

1 : 4-Dichloroanthraquinone-α-sulphonic acid gives a *trichloroanthraquinone*, melting at 253—254°. A *dichlorobromoanthraquinone*, m. p. 233°, is produced by the action of bromine and water at 190° on sodium 1 : 4-dichloroanthraquinone-β-sulphonate. F. M. G. M.

Preparation of Halogenated Nitroanthraquinones. FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 214150).—The nitroanthraquinonesulphonic acids, like the anthraquinonesulphonic acids, yield halogenated derivatives when treated with aqueous chlorine, the sulphonic group being eliminated in each case.

1-*Chloro*-5-*nitroanthraquinone* is prepared from sodium 1 : 5-nitroanthraquinonesulphonate by treatment with sodium chlorate and hydrochloric acid; it forms pale yellow needles. 1 : 6-, 1 : 7-, and 1 : 8-*Chloronitroanthraquinones* were similarly obtained, and the colours of their solutions in various solvents are tabulated in the patent.

F. M. G. M.

[Preparation of Thioglycine Derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 213960. Compare Abstr., 1909, i, 496, 941).—The action of the previously-described thiolanthraquinones on chloroacetylaminoanthraquinones leads to the formation of anthraquinonethioglycines having the general formula (A = anthraquinone) $A\cdot S\cdot CH_2\cdot CO\cdot NH\cdot A$.

The following components and their condensation products are described in the patents:

Chloroacetyl-1-*aminoanthraquinone*, greenish-yellow needles, and its condensation *products* with α- and β-thiolanthraquinones.

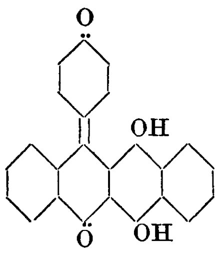
Chloroacetyl-1-*amino*-4-*hydroxyanthraquinone*, orange-red needles, and the *products* of its condensation with α-thiolanthraquinone and with 1 : 5-dithiolanthraquinone.

Chloroacetyl-1 : 4-*diaminoanthraquinone*, yellowish-brown prisms, and its *compound* with α-thiolanthraquinone.

Chloroacetyl-1 : 5-*diamino*-4 : 8-*dihydroxyanthraquinone*, and its condensation *product* with α-thiolanthraquinone. F. M. G. M.

The Naphthacene Series. III. HUGO VOSWINCKEL and FRITZ DE WEERTH (*Ber.*, 1909, **42**, 4648—4650. Compare Abstr., 1906, i, 99; 1909, i, 166).—When naphthacenediquinone, acetic acid, and an excess

of sulphuric acid are heated to a higher temperature than is required for the preparation of 6 : 11-dihydroxy-6-acetoxy-11-*p*-hydroxyphenyldihydronaphthacenequinone, the chief product is 5 : 12-*dihydroxy*-11-*phenonaphthacenequinone* (annexed formula), which crystallises in dark red, pointed prisms, soluble in dilute sodium hydroxide or in concentrated sulphuric acid to red solutions. The diacetyl derivative, $C_{24}H_{12}O_4Ac_2$, has m. p. 264°. The same quinone is formed when the primary condensation product (dihydroxyacetoxy-hydroxyphenyldihydronaphthacenequinone) is heated with acetic and sulphuric acids; the reduction then proceeds at the expense of part of the quinone, and the product $C_{24}H_{16}O_5$, m. p. 174° (Abstr., 1909, i, 167) is also obtained.



5 : 12-*Dihydroxy*-6-*keto*-11-*hydroxyphenyl*-6 : 11-*dihydronaphthacene*,

$$C_6H_4<\begin{matrix}CH(C_6H_4\cdot OH)\cdot C\cdot C(OH)\\ CO\text{------------}\overset{||}{C}\cdot C(OH)\end{matrix}>C_6H_4,$$

obtained by reducing the phenodihydroxynaphthacenequinone with an alkaline solution of sodium hyposulphite, separates as an orange-coloured, crystalline powder, m. p. 225°. The *triacetate*, $C_{24}H_{13}O_4Ac_3$, forms a pale yellow, crystalline powder, m. p. 206—210°. When the quinone is reduced with zinc dust and glacial acetic acid, a *product*, $C_{24}H_{16}O_3$, is obtained as a pale yellow, crystalline powder with no definite m. p. Its *acetyl* derivative, $C_{26}H_{18}O_4$, has m. p. 171°.

J. J. S.

Stereo- and Structural Isomerides obtained by the Introduction of Acyl Radicles into β-Hydroxylamines. I. GUIDO CUSMANO (*Gazzetta*, 1909, **39**, ii, 336—346).—The author describes observations on the action of acyl chlorides on β-hydroxylamines, and shows that this reaction affords a means of obtaining substituted hydroxy-iminic acids.

The compound described by Beckmann and Pleissner (Abstr., 1891, 936) as pulegonehydroxylamine benzoate, m. p. 137—138°, which may be prepared by the action of benzoyl chloride on pulegonehydroxylamine in ether, is, in reality, anti-*menthonylbenzhydroximic acid*, $\begin{matrix}Ph\cdot C\cdot O\cdot C_{10}H_{17}O\\ OH\cdot \overset{||}{N}\end{matrix}$, $[\alpha]_D^{20}$ −20·14° (in alcohol); in freezing acetic acid it has the normal molecular weight, and when treated with sodium ethoxide, it yields sodium benzhydroxamate and pulegone.

syn-*Menthonylbenzhydroximic acid*, $\begin{matrix}Ph\cdot C\cdot O\cdot C_{10}H_{17}O\\ \overset{||}{N}\cdot OH\end{matrix}$, prepared by the action of concentrated hydrochloric acid on the *anti*-compound, or by varying the conditions under which benzoyl chloride and pulegonehydroxylamine react, has m. p. 182°, $[\alpha]_D^{22}$ −42·44° (in methyl alcohol), and exhibits normal cryoscopic behaviour in acetic acid. Its *hydrochloride*, m. p. 58° (decomp.), is converted at 100° into an oil, which, with sodium carbonate, yields benzhydroxamic and benzoic

acids and a *substance*, m. p. 84°, soluble in hydrochloric acid with formation of *syn*-menthonylbenzhydroximic acid.

The *menthonyl ether* of *benzhydroxamic acid*, $\begin{matrix} Ph\cdot C\cdot OH \\ \| \\ N\cdot OC_{10}H_{17}O \end{matrix}$, obtained, together with *syn*-menthonylbenzhydroximic acid, by the action of gaseous hydrogen chloride on the *anti*-acid suspended in ether, forms plates, m. p. 96°, and may be converted into *syn*-menthonylbenzhydroximic acid by the action of hydrochloric acid.

T. H. P.

Syntheses in the Camphor and Terpene Series. II. Complete Synthesis of Camphoric Acid and Camphor. Gustav Komppa (*Annalen*, 1909, **370**, 209—233. Compare Abstr., 1909, i, 726).—The present communication contains a detailed account of the synthesis of camphoric acid from *apo*camphoric acid, thereby establishing the validity of Bredt's camphor formula.

When diketo*apo*camphoric acid (1 mol.) is treated with methyl iodide (2 mols.) and sodium methoxide (2 mols.) in methyl-alcoholic solution, it yields a mixture of methyl diketocamphorate and methylketomethoxydehydrocamphorate, which is resolved by treatment with an aqueous solution of sodium carbonate, in which the first named is soluble. *Methyl diketocamphorate*, $\begin{matrix} CO\cdot CMe(CO_2Me) \\ | \\ CO-CH(CO_2Me) \end{matrix}\!\!>\!CMe_2$, crystallises in stout plates, m. p. 85—88°; the *copper* salt, $C_{24}H_{30}O_{12}Cu$, crystallises in stellate groups of bluish-green prisms; the acid is reduced in aqueous solution by sodium amalgam, yielding 4:5-*dihydroxycamphoric acid*, obtained as a viscid, yellow syrup; the *silver*, $C_{10}H_{14}O_6Ag$, and *barium* ($1H_2O$) salts are amorphous, white powders.

2 : 2 : 3-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid*,

$$\begin{matrix} CH_2\cdot CMe(CO_2H) \\ | \\ CH{=\!=\!=}C(CO_2H) \end{matrix}\!\!>\!CMe_2,$$

is obtained by reducing 4:5-dihydroxycamphoric acid with hydriodic acid and red phosphorus, also by hydrolysing the ester resulting from the action of diethylaniline on ethyl α-bromocamphorate; it crystallises in small, colourless, monoclinic prisms, m. p. 221—223°, and is converted by a solution of hydrogen bromide in glacial acetic acid at 120—125° under pressure into *β-bromocamphoric acid*, obtained as an oil, which, when acted on by zinc dust and glacial acetic acid, yields a mixture of camphoric and *iso*camphoric acids. The *semi-anilide* of *r*-camphoric acid, $C_{16}H_{21}O_3N$, prepared by the action of aniline on *r*-camphoric acid in alcoholic solution, crystallises in small, rhombohedra or long needles, m. p. 214·5°—215·5° (corr.).

Methyl 4-*keto*-5-*methoxydehydrocamphorate*,

$$\begin{matrix} C(OMe){:}C(CO_2Me) \\ | \\ CO-CMe(CO_2Me) \end{matrix}\!\!>\!CMe_2,$$

is an ether-like oil, b. p. 156—157°/8 mm., $D_{17\cdot5}^{17\cdot5}$ 1·188, n_D 1·49212, which, when reduced with sodium amalgam and methyl alcohol, yields the corresponding hydroxy-acid, from which dehydrocamphoric acid is obtained by treatment with hydriodic acid and red phosphorus.

W. H. G.

Condensation Products from Camphor. MARCEL GUERBET (*Compt. rend.*, 1909, **149**, 931—933.* Compare Abstr., 1909, i, 310). —The formation of neutral, oily products when the mixture resulting from the action of sodium on a solution of camphor in toluene is heated at 280° has been observed by Montgolfier (Abstr., 1878, 891), who supposed them to have the composition $(C_{10}H_{10})_n$. The oil has now been distilled, and from the fraction b. p. 326—335° two condensation products isolated.

(i) *Bornylenecamphor*, $C_8H_{14}<\begin{array}{c}C{=}C{-}\\ |\quad\ |\\ CO\ CH_2\end{array}>C_8H_{14}$ occurs as colourless needles, m. p. 93°, $[\alpha]_D$ + 69·2° in alcohol. It unites with hydrogen bromide, forming a *compound*, $C_{20}H_{31}OBr$, m. p. 202—203°. Bromine attacks it, liberating hydrogen bromide and yielding *bromobornylenecamphor*, $C_{20}H_{29}OBr$, m. p. 101°. Warm fuming nitric acid converts bornylenecamphor into a *nitro*-derivative, $C_{20}H_{29}O\cdot NO_2$, which crystallises in colourless, rhombic tablets, m. p. 204°, and forms a *sodium* salt, $C_{20}H_{28}ONa\cdot NO_2,3H_2O$, occurring as pearly leaflets.

(ii) *Bornylcamphor*, $C_8H_{14}<\begin{array}{c}CH\cdot CH\\ |\quad\ |\\ CO\ CH_2\end{array}>C_8H_{14}$, crystallises in needles, m. p. 77·5°, and can also be prepared by the reduction of benzylidenecamphor by sodium amalgam in acid alcoholic solution.

W. O. W.

Composition of Oil of Turpentine. EUGÈNE DARMOIS (*Compt. rend*, 1909, **149**, 730—733. Compare Abstr., 1908, ii, 747).—A further application of measurements of rotatory dispersion to the determination of the composition of optically active hydrocarbons. Dextrorotatory turpentine contains *d*-pinene, together with a hydrocarbon showing feebly lævorotatory dispersive power and having $[\alpha]_D - 21·7°$. The latter appears also to be present in French lævo-oils, and may be identical with nopinene. The b. p. of the oil from *Pinus halepensis* remains constant at 155° for 90% of the product; the distillate shows strong dispersion, and has $[\alpha]_D$ + 82·8°, m. p. − 50°.

By the application of Biot's law of mixtures as previously indicated, the proportion of pinene in French lævo-oils and in Algerian dextro-oils is found to be 62%. W. O. W.

Hydrogenation in the Terpene Series. G. VAVON (*Compt. rend.*, 1909, **149**, 997—999).—Pinene rapidly absorbs hydrogen in presence of platinum-black. In this way the α-pinene (Algerian) prepared by Darmois (preceding abstract) has furnished, in quantitative yield, a *hydrocarbon*, $C_{10}H_{18}$, b. p. 166°/755 mm., $[\alpha]_D$ + 22·7°, D_{15}^{15} 0·861, solidifying at about − 45°. It differs from the hydrocarbon described by Sabatier and Senderens (Abstr., 1901, i, 459) in remaining unaltered on exposure to air. Under the same conditions, French *l*-pinene yields the same compound, but having $[\alpha]_D - 21·3°$; α- and β-pinene therefore appear to yield the same substance on hydrogenation.

Camphene forms a *hydrocarbon*, $C_{10}H_{18}$, m. p. about 87°, which is not identical with that obtained by Sabatier and Senderens (*loc. cit.*)

* and *J. Pharm. Chim.*, 1910, [vii], **1**, 5—10.

by the action of water on the magnesium derivative of camphene hydrochloride.

Limonene, $[\alpha]_D$ +121·3°, combines with 4H, giving an inactive *hydrocarbon*, b. p. 169°, D_{15}^{15} 0·803. Maleic, fumaric, cinnamic, and erucic acids have been hydrogenated in the same way. W. O. W.

[α-Terpinene.] KARL AUWERS. (*Ber.*, 1909, **42**, 4427—4429. Compare Abstr., 1909, i, 592).—Polemical. A reply to Semmler (Abstr., 1909, i, 942). R. V. S.

Constituents of Ethereal Oils. I. Terpinolene. II. Terpinene. FRIEDRICH W. SEMMLER and ENDRE SCHOSSBERGER (*Ber.*, 1909, **42**, 4644—4647).—I. Pure terpinolene is best prepared by the action of zinc dust on an ethereal-alcoholic solution of the pure tetrabromide, m. p. 115—116°. When acetic acid is used, the product always contains appreciable amounts of terpinene. Pure terpinolene has b. p. 67—68°/10 mm., D^{20} 0·854, and n_D 1·484.

II. Terpinene. Polemical (compare Auwers, preceding abstract). J. J. S.

Cryptomeria Japonica Oil. H. KIMURA (*Ber. Deut. pharm. Ges.*, 1909, **19**, 369—387).—The oil distilled from the wood of this tree is shown to consist to the extent of 60% of the sesquiterpenes, *l*-cadinene and suginene, the residue being a sesquiterpene alcohol, cryptomeriol (compare Kimoto, *Chem. Centr.*, 1902, ii, 382; Keimatsu, *Pharm. J.*, 1905, 189).

On steam distillation the wood yields 1·5% of a yellow oil, which darkens and thickens on standing. The re-distilled oil has D 0·9590, $[\alpha]_D$ −22°32′, contains no methoxyl, nitrogen, sulphur, or halogens, and is free from acids, aldehydes, and phenols.

The terpene portion was separated by treating the original oil with metallic sodium or potassium. It consisted of a mixture of sesquiterpenes, which was resolved into its components by treatment with hydrogen chloride, which furnished a solid and a liquid dihydrochloride. The former had m. p. 117—118° and $[\alpha]_D$ −37°4′ in chloroform, and proved to be identical with *l*-cadinene dihydrochloride from cade oil. The liquid hydrochloride on treatment with sodium acetate and acetic acid regenerated a new sesquiterpene, *suginene*, D 0·918, $[\alpha]_D$ −10°34′, which yields a liquid *dihydrobromide*, b. p. 140—150°/16 mm., D 0·988, $[\alpha]_D$ −11°15′. The sesquiterpene regenerated from this had D 0·921 and $[\alpha]_D$ +14°43′, whilst that regenerated from the liquid *dihydriodide* had D 0·911 and $[\alpha]_D$ −24°21′. No crystalline derivatives of suginene could be obtained, but it appears to be oxidised to an alcohol by treatment with bromine water.

The alcoholic portion of the oil was isolated by treatment with potassium wire, the sesquiterpene portion being then removed by distillation under reduced pressure. The potassium derivative was freed from excess of potassium and other impurities by solution in ether. The potassium derivative, on treatment with water, furnished *cryptomeriol*, $C_{15}H_{25}\cdot OH$, b. p. 162—163°/10 mm., D 0·964,

$[\alpha]_D$ $-37°5$, a thick, colourless oil. The potassium derivative of this, when treated with carbon disulphide, yielded a *xanthic* ester,

$$C_{15}H_{25}O \cdot CS \cdot SK,$$

which on addition of water did not regenerate the original alcohol, but colourless, crystalline iso*cryptomeriol*, $C_{15}H_{26}O$, m. p. 135—136°, and a new liquid *alcohol*, $[\alpha]_D$ $-3°25'$. On treatment with formic acid, cryptomeriol yielded a *sesquiterpene*, D 0·918, b. p. 143—144°/13 mm., $[\alpha]_D$ $-1°5'$, and with phosphoric oxide, a second *sesquiterpene*, D 0·917, $[\alpha]_D$ $+56°26'$, which was also prepared from the first sesquiterpene by the action of phosphoric oxide. Both gave liquid products with gaseous halogen acids.

Cadinene cannot be regenerated unchanged from its compounds with the halogen acids. T. A. H.

Volatile Oil of Rhus Cotinus ("Young Fustic"). Gustave Perrier and A. Fouchet (*Bull. Soc. chim.*, 1909, [iv], **5**, 1074—1075).—The leaves and twigs on steam distillation yield 0·1% of a colourless, volatile oil with an odour somewhat recalling that of oil of turpentine. The oil has D^{15} 0·875, n_D 1·4693, $[\alpha]_D$ $+13°$, is completely soluble in alcohol of 94°, is acid to litmus, contains free alcohols, and gives the aldehyde reaction with Schiff's reagent. T. A. H.

Catalytic Oxidation of Guaiacum Resin by Copper. Hector A. Colwell (*J. Physiol.*, 1909, **39**, 358—360).—Both metallic copper and its salts have a catalytic oxidising action on guaiacum, which is remarkable among the other metals examined for its intensity.

W. D. H.

Preparation of Indican. Henri ter Meulen (*Rec. trav. chim.*, 1909, **28**, 339—341).—In a previous paper (Abstr., 1900, i, 404) the author has shown with Hoogewerff, that indican may be prepared conveniently from plants containing it, by extraction with boiling water, but Perkin and Bloxam have stated recently (Trans., 1907, **91**, 1715) that in their experience extraction with water gives a smaller yield of indican than is obtained with acetone as a solvent.

The author has repeated the previous work with material supplied to him by Perkin and Bloxam, and finds that, using his modified process (*Rec. trav. chim.*, 1905, **24**, 468), he obtains 2·7% of indican as compared with 3·166% found by Perkin and Bloxam, so that extraction with hot water does not necessarily involve any material loss of glucoside. T. A. H.

Active Principle of a Benin Spear Poison. Patrick P. Laidlaw (*J. Physiol.*, 1909, **39**, 354—357).—The supply of poison was obtained from two spear heads from Benin. Although attempts to prepare a pure crystalline toxic substance failed, owing to impurities, there is no doubt that the poison is a glucoside which has the solubilities and physiological properties of strophanthin; it also gives the characteristic colour reaction of that substance. W. D. H.

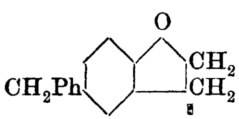
Discovery of the Optical Activity of Tannin. EDMUND O. VON LIPPMANN (*Ber.*, 1909, **42**, 4678—4679. Compare Rosenheim, Abstr., 1909, i, 599).—C. Scheibler (*Zeitsch. Zuckerind.*, 1866, **16**, 33) appears to have been the first to draw attention to the optical activity shown by certain specimens of tannin. J. J. S.

Furfurylpropylcarbinol. Mlle. EUGÈNIE JOLKVER (*Rec. trav. chim.*, 1909, **28**, 439—443).—*Furfurylpropylcarbinol*,

$$C_4OH_3\cdot CHPr^{a}\cdot OH,$$

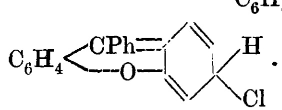
b. p. 92—93°/12 mm. or 195—198°/760 mm., prepared by Grignard's method (Abstr., 1901, i, 680) from magnesium propyl bromide and furfuraldehyde, is a colourless liquid, which becomes yellow on exposure to light. The corresponding *chloride* has b. p. 90—91°/6 mm. or 94—95°/10 mm., and the *acetate*, b. p. 96—97°/22 mm. or 106°/28 mm., is a colourless, mobile liquid of pleasant odour. T. A. H.

4-Benzylcumaran. CHARLES MARSCHALK (*Ber.*, 1909, **42**, 4485—4487). — 4-*Benzylcumaran* (annexed formula), prepared by the reduction of 4-benzoylcumaran (compare Abstr., 1907, i, 950) by means of sodium and alcohol, forms white crystals, m. p. 61°, and dissolves in concentrated sulphuric acid, giving a yellow solution, which becomes green on addition of ferric chloride. This compound is presumably the mother substance of the catechin group. T. H. P.



Triphenylmethyl. XVIII. Quinocarbonium Salts. MOSES GOMBERG and LEE H. CONE (*Annalen*, 1909, **370**, 142—208. Compare Abstr., 1907, i, 504; 1909, i, 144).—A complete parallelism is shown to exist between the salts of triphenylcarbinol and its derivatives and the salts of xanthenol and analogous substances, from which the conclusion is drawn that the compounds which have been regarded previously as carboxonium salts (compare Kehrmann, Abstr., 1900, i, 61; Werner, Abstr., 1902, i, 50) are really carbonium salts, and, like triphenylcarbinol chloride, capable of existing in a benzenoid (I) and a quinonoid (II and III) form:

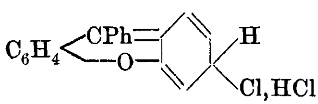
$$\text{I.}\quad O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPh\cdot Cl \qquad \text{II.}\quad O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:C_6H_4<\begin{matrix}H\\Cl\end{matrix}$$

III. 

When hydrogen chloride is passed into a solution of xanthenol in an indifferent solvent, a yellow precipitate is obtained, which is a hydrochloride of xanthenol chloride (quinoxanthenol chloride hydrochloride); the mol. of hydrogen chloride may be removed by suitable treatment, leaving a colourless chloride. The normal, colourless xanthenol chlorides are very similar in their chemical behaviour to triphenylcarbinol chloride. They give yellow solutions when dissolved in liquid sulphur dioxide, showing that they exist in two tautomeric

forms, a further proof of which is shown by the behaviour of phenyl-*p*-bromoxanthenol bromide, which when treated with silver chloride yields phenyl-*p*-chloroxanthenol chloride.

The formation of coloured derivatives is induced, not only by sulphur dioxide and hydrogen chloride, but also by metallic halides, sulphuric acid, and perchloric acid. The last-mentioned acid forms stable, crystalline salts, not only with xanthenol derivatives, but also with those of triphenylmethane, which latter do not contain oxygen. The colour of these salts cannot be due, therefore, to the formation of oxonium salts.



Phenylxanthenol (compare Bünzly and Decker, Abstr., 1904, i, 912) when treated in chloroform with a solution of acetyl chloride and subsequently with hydrogen chloride yields *phenylquinoxanthenol chloride hydrochloride* (annexed formula), crystallising in glistening, reddish-orange prisms; the *chloride*, $O{:}(C_6H_4)_2{:}CPhCl$, is obtained by passing air through a solution of the hydrochloride just described at about 50—60° in the complete absence of water; it crystallises in colourless prisms, m. p. 105—106°. A solution of the chloride in benzene (1) when heated under pressure with silver yields an *unsaturated* compound, which, in analogy to triphenylmethyl, absorbs oxygen quite readily, yielding *phenylxanthenol peroxide*, $\left[O{<}{}^{C_6H_4}_{C_6H_4}{>}CPh\right]_2O_2$, transparent, colourless, glistening leaflets, m. p. 219° (decomp.), and (2) when treated with magnesium benzyl chloride yields *αβ-diphenyl-α-xanthylethane*, $O{:}(C_6H_4)_2{:}CPh{\cdot}CH_2Ph$, colourless, rhombic prisms, m. p. 169°. The following additive compounds of the chloride have been prepared: *ferrichloride*, $C_{19}H_{13}OCl,FeCl_3$, brownish-red spangles, sinters at 167°, m. p. 170°; *mercurichloride*,

$$C_{19}H_{13}OCl,HgCl_2,$$

white powder, sinters at 230°, m. p. 248—250° (decomp.); *perbromide*, $C_{19}H_{13}OCl,Br_2$, unstable, orange-yellow powder, sinters at 146°, m. p. 150° (decomp.); *periodide*, $C_{19}H_{13}OCl,I_2$, brownish-red, crystalline powder; *perchloride*, $C_{19}H_{13}OCl,Cl_2$, orange-red needles. *Phenylxanthenol hydrogen sulphate*, $C_{19}H_{13}O{\cdot}SO_4H$, forms stellate aggregates of orange crystals, m. p. 175°; the *perchlorate*, $C_{19}H_{13}O{\cdot}ClO_4$, obtained by the action of silver perchlorate on the chloride or directly from perchloric acid and phenylxanthenol, crystallises in golden, transparent prisms, m. p. 281—282°.

The following compounds are obtained by methods similar to those just described.

p-*Tolylxanthenol*, $O{<}{}^{C_6H_4}_{C_6H_4}{>}C{<}{}^{C_6H_4Me}_{OH}$, prepared from xanthone and *p*-iodotoluene, crystallises in groups of small, transparent plates, m. p. 150°. p-*Tolylquinoxanthenol chloride hydrochloride*,

$$O{<}{}^{C_6H_4\text{———————}}_{C_6H_4(Cl,HCl)}{>}C{\cdot}C_7H_7,$$

is an unstable, brown, crystalline substance. The *chloride*,

$$O{:}(C_6H_4)_2{:}C(C_7H_7)Cl,$$

crystallises in colourless prisms, m. p. 131°; *ferrichloride*,

$$C_{20}H_{15}OCl,FeCl_3,$$

yellowish-brown crystals, sinters at 205°, m. p. 211°; *zinc chloride*, $C_{20}H_{15}OCl,ZnCl_2$, brownish-yellow needles, sinters at 233°, m. p. 240—247° (decomp.); *perbromide*, $C_{20}H_{15}OCl,Br_2$, amorphous, brownish yellow powder; the *perchlorate*, $C_{20}H_{15}O\cdot ClO_4$, crystallises in yellow needles, m. p. 239°. p-*Tolylxanthenol peroxide*, $C_{40}H_{30}O_4$, forms colourless, glistening prisms, m. p. 212° (decomp.).

Phenyldinaphthoxanthenol, $O{<}{\substack{C_{10}H_6\\C_{10}H_6}}{>}CPh\cdot OH$, prepared by oxidising benzylidene-β-dinaphthyl oxide in glacial acetic acid with lead peroxide, has m. p. 265—268°. *Phenyldinaphthoquinoxanthenol chloride hydrochloride*, $C_{27}H_{18}OCl_2$, crystallises in long, dark red, glistening needles, loses hydrogen chloride when heated, becomes white at 230°, m. p. 270—274°. *Phenyldinaphthoxanthenol chloride*, $C_{27}H_{17}OCl$, forms almost colourless crystals, m. p. 274°; the *ferrichloride*, $C_{27}H_{17}OCl,FeCl_3$, dark red needles; *stannichloride*, $C_{27}H_{17}OCl,SnCl_4$, red crystals, and *zinc chloride*, $C_{27}H_{17}OCl,ZnCl_2$, glistening, red needles, were analysed; the *hydrogen sulphate*, $C_{27}H_{17}O\cdot SO_4H,\frac{1}{2}H_2SO_4$, forms long, red needles, m. p. 145—150°; the *perchlorate*, $C_{27}H_{17}O\cdot ClO_4$, crystallises in scarlet leaflets with a golden shimmer, and does not melt at 280°.

p-*Methoxyphenyldinaphthoquinoxanthenol chloride hydrochloride*,

$$C_{28}H_{19}O_2Cl,HCl,$$

forms dark red, glistening crystals, m. p. 235° (decomp.). p-*Methoxyphenyldinaphthoxanthenol chloride*, $O{:}(C_6H_4)_2{:}C(C_6H_4\cdot OMe)Cl$, forms white crystals; the red, crystalline *additive* products with ferric chloride, m. p. 235—237°, stannic chloride, zinc chloride, and iodine were analysed; the *hydrogen sulphate*, $C_{28}H_{19}O_2\cdot SO_4H,\frac{1}{2}H_2SO_4$, bright red needles, m. p. 145°, and *perchlorate*, $C_{28}H_{19}O_2\cdot ClO_4$, were analysed.

p-*Chlorophenylxanthenol*, $O{:}(C_6H_4)_2{:}C(C_6H_4Cl)\cdot OH$, has m. p. 173°; the *chloride*, $C_{19}H_{12}OCl_2$, forms colourless, transparent prisms, m. p. about 104—105°, and when treated with alcohol yields p-*chlorophenylxanthenol ethyl ether*, $C_{21}H_{17}O_2Cl$, crystallising in tufts of colourless crystals, m. p. 120—121°; the *additive* compounds of the chloride with ferric chloride, m. p. 209—210°, zinc chloride, and bromine, m. p. 166° (decomp.), were analysed; they are orange-red, crystalline powders. p-*Chlorophenylxanthenol peroxide*, $C_{38}H_{24}O_4Cl_2$, prepared by the action of silver and air on a solution of the chloride in benzene, crystallises with benzene in colourless, glistening prisms, m. p. 213° (decomp.). p-*Chlorophenylquinoxanthenol chloride hydrochloride*,

$$C_{19}H_{12}OCl_2,HCl,$$

forms brownish-yellow needles.

p-*Bromophenylxanthenol*, $C_{19}H_{13}O_2Br$, crystallises in long, colourless, pointed needles, m. p. 183°; the *chloride*, $C_{19}H_{12}OBrCl$, forms transparent, colourless prisms, m. p. 118—119°; the *perchlorate*,

$$C_{19}H_{12}OBr\cdot ClO_4,$$

is a crystalline, orange powder, sinters at 295°, m. p. about 310° p-*Bromophenylquinoxanthenol chloride hydrochloride*, $C_{19}H_{12}OClBr,HCl$, crystallises in yellow needles. p-*Bromophenylxanthenol peroxide*,

$$C_{38}H_{24}O_4Br_2,$$

crystallises in colourless, rhombic plates, m. p. 210—211° (decomp.).

Phenyl-p-*chloroxanthenol*, $O{<}{\substack{C_6H_3Cl\\C_6H_4}}{>}CPh\cdot OH$, prepared from

4-chloroxanthone and magnesium phenyl bromide, crystallises in slender leaflets, m. p. 164°; the *chloride*, $C_{19}H_{12}OCl_2$, crystallises in rosettes of colourless rods, m. p. 151°. *4-Chloroxanthone* was prepared as follows: 2 : 4-dichloroaniline is converted into 2 : 4-dichlorobenzonitrile, colourless prisms, m. p. 61°, which when hydrolysed yields 2 : 4-dichlorobenzoic acid, m. p. 164°; the latter substance when treated with sodium phenoxide and copper powder yields 4-chloro-2-phenoxybenzoic acid, m. p. 171°, which is converted by warm concentrated sulphuric acid into 4-chloroxanthone, m. p. 130°. The compound, m. p. 171°, described by Ullmann and Wagner is probably an isomeride (compare Abstr., 1907, i, 846). *Phenyl-p-chloroquinoxanthenol chloride hydrochloride*, $C_{19}H_{12}OCl_2,HCl$, is an extremely unstable, red, crystalline substance.

Phenyl-p-bromoxanthenol, $C_{19}H_{13}O_2Br$, prepared by way of *4-bromo-2-phenoxybenzoic acid*, $C_{13}H_9O_3Br$, crystallising in rosettes of needles, m. p. 178°, and *4-bromoxanthone*, colourless needles, m. p. 126°, is obtained in colourless crystals, m. p. 145°; the *bromide*, $C_{19}H_{12}OBr_2$, crystallises in almost colourless needles, m. p. 155°. *Phenyl-p-bromoquinoxanthenol bromide hydrobromide*, $C_{19}H_{12}OBr_2,HBr$, crystallises in orange-red prisms with a blue reflex.

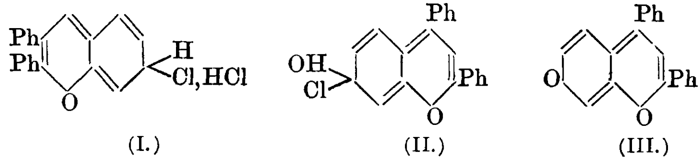
II. *Hydrochlorides and Perchlorates in the Triphenylmethane Series.*—Phenyldi-*p*-anisylcarbinol chloride combines with hydrogen chloride, forming a *hydrochloride*, $OMe\cdot C_6H_4\cdot CPh\colon C_6H_4(OMe)Cl,HCl$, obtained as a dark red oil. *Tri-p-anisylcarbinolchloride hydrochloride*,

$$C(C_6H_4\cdot OMe)_2\colon C_6H_4(OMe)Cl,HCl,$$

crystallises in dark red needles with a blue reflex (compare Baeyer and Villiger, Abstr., 1903, i, 811).

The *perchlorates* of the following compounds have been prepared and analysed: triphenylcarbinol, $C_{19}H_{15}\cdot ClO_4$, red crystals, m. p. 150°; diphenyl-*p*-tolylcarbinol, $C_{20}H_{17}\cdot ClO_4$, brown crystals; tri-*p*-tolylcarbinol, $C_{22}H_{21}\cdot ClO_4,\frac{1}{2}C_6H_5\cdot NO_2$, glistening, violet crystals, m. p. 187°; *p*-chlorotriphenylcarbinol, $C_{19}H_{14}Cl\cdot ClO_4$, compact, red crystals, m. p. 142—144°; *p*-bromotriphenylcarbinol, red crystals with a blue reflex, m. p. 151°; tri-*p*-chlorotriphenylcarbinol, small, brownish-red plates with a violet reflex, m. p. 172—174°; tri-*p*-bromotriphenylcarbinol, $C_{19}H_{12}Br_3\cdot ClO_4$, dark brownish-red crystals, m. p. 174—175°; diphenyl-*p*-anisylcarbinol, $C_{20}H_{17}O\cdot ClO_4$, red needles, m. p. 192°; phenyldi-*p*-anisylcarbinol, dark red needles, m. p. 112—113°; tri-*p*-anisylcarbinol, $C_{22}H_{21}O_3\cdot ClO_4$, dark purple needles, m. p. 195°.

III. *Derivatives of Benzo-γ-pyrone.*—The pyranols are regarded as being strictly analogous to the xanthenols, the coloured pyranol salts being quinocarbonium salts (compare Decker, Abstr., 1907, i, 1064).



(I.) (II.) (III.)

2 : 3-*Diphenylbenzopyranol chloride hydrochloride* (formula I) crystallises in long, yellow needles.

[With O. B. WINTER.]—7-*Hydroxy*-2 : 4-*diphenylbenzopyranol chloride hydrochloride*, $C_{21}H_{16}O_2Cl_2$, forms orange-red crystals; it loses 1HCl when dry air is passed through the solution in chloroform, yielding the orange-yellow quinonoid *chloride* (formula II); if the solution be heated, another mol. of hydrogen chloride is evolved, with the formation of the *quinone* (formula III), an amorphous, red powder.

IV. *Acridine Derivatives.*—The salts of the phenylacridols are probably quinocarbonium salts of the same type as the coloured salts of phenylxanthenol.

5 : 10-*Diphenylacridol chloride hydrochloride*,

$$NPh{<}\begin{matrix}C_6H_4(Cl,HCl)\\C_6H_4\end{matrix}{>}CPh,$$

crystallises in golden needles; the *chloride*, $C_{25}H_{18}NCl$, prepared by the action of acetyl chloride on 5 : 10-diphenylacridol, crystallises with $1Me{\cdot}CO_2H$ and $2C_6H_6$ in yellow crystals, and with $2CHCl_3$ in yellow plates; it is also obtained by heating the hydrochlride in a vacuum at 150°, and does not melt at about 300°. W. H. G.

3 : 6-Dimethylfluoran. ENOS FERRARIO and M. NEUMANN (*Bull. Soc. chim.*, 1909, [iv], 5, 1098—1101. Compare Lambrecht, Abstr., 1909, i, 949).—3 : 6-Dimethylfluoran, m. p. 213·5° (corr.), has been obtained by the action of phthalyl chloride on *m*-cresol, and also in 80% yield by heating phthalic anhydride with *m*-cresol and zinc chloride. The compound is readily esterified by heating with alcoholic hydrogen chloride; on the addition of platinic chloride, the *platinichloride*, $(C_{21}H_{16}OCl{\cdot}CO_2Et)_2PtCl_4$, separates. The *methyl* ester, $C_{21}H_{17}O{\cdot}CO_2Me$, has m. p. 115—116°.

The addition of bromine to a solution of dimethylfluoran in acetic acid results in the formation of an unstable, red oxonium *tribromide*. A *dibromo*-derivative, m. p. 249—250°, and a *tetrabromo*-derivative, m. p. 306°, have also been obtained. Dimethylfluoran forms a *tetranitro*-derivative, $C_{22}H_{12}O_{11}N_4$, and possibly a *dinitro*-derivative, m. p. 242°. The former decomposes at about 280°, and on reduction yields an amine, the *picrate* of which decomposes at 120—121°. W. O. W.

Preparation of 2 : 3-Diketodihydro-(1)-thionaphthen Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 213458. Compare Abstr., 1909, i, 950).—2 : 3-*Diketodihydro*-1-*thionaphthen*-2-*oxime* is prepared by adding sodium nitrite to a cooled solution of 3-oxy-1-thionaphthen in aqueous sodium hydroxide and subsequent acidification with dilute sulphuric acid. It forms yellow, silky prisms, m. p. 168°. The *acetyl* derivative, m. p. 168°, and the *phenylhydrazone*, m. p. 154°, are described.

On hydrolysing the preceding compound with 15% hydrochloric acid and reducing the colourless product with iron filings, it yields 2 : 3-diketodihydro-1-thionaphthen, the *phenylhydrazone* of which has m. p. 162°, and the *dianilino*-derivative, m. p. 80°.

The higher homologues of the foregoing compounds are similarly prepared, 3-*oxy*-5-*methyl*-(1)-*thionaphthen* yielding 2 : 3-*diketo*-5-*methyl*-

dihydro-(1)-thionaphthen-2-oxime, m. p. 185°, and *5-chloro-3-oxy-(1)-thionaphthen* gives *5-chloro-2 : 3-diketodihydro-1-thionaphthen-2-oxime*, m. p. 188°. F. M. G. M.

Preparation of Derivatives of 2:3-Diketodihydro-(1)-thionaphthens. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 214781).—Derivatives of 2 : 3-diketodihydro-(1)-thionaphthen have formerly been obtained by the action of aromatic amines on the dihalogenated derivatives of 3-ketodihydro-(1)-thionaphthen and hydrolysis of the product. It has now been found that nitroso-derivatives of aromatic amines will condense with 3-oxy-(1)-thionaphthen itself, giving rise to a condensation product which, on hydrolysis, furnishes the diketo-compound.

3-Oxy-(1)-thionaphthen in alcoholic or dilute alkali solution condenses at 40° with *p*-nitrosodimethylaniline, giving the *compound* (m. p. 176°), $C_6H_4<\substack{S\\CO}>C:N\cdot C_6H_4\cdot NMe_2$. This product, when hydrolysed with 15% hydrochloric acid, gives 2 : 3-diketodihydro-(1)-thionaphthen.

p-Nitrosoethylaniline and *p*-nitrosodiphenylamine give similar products, melting at 158° and 193° respectively, which also undergo hydrolysis to furnish the diketone.

3-Oxy-5-methyl-(1)-thionaphthen, when submitted to this series of operations, yields 2 : 3-diketo-5-methyldihydro-1-thionaphthen, m. p. 143°. F. M. G. M.

Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Para-Position. WILHELM AUTENRIETH and FRITZ BEUTTEL (*Ber.*, 1909, **42**, 4346—4357).—It has been shown recently that dihydric mercaptans readily condense with aldehydes or ketones to form compounds containing six-, seven-, or sixteen-membered heterocyclic systems containing sulphur. The ease with which *o*-xylylene hydrosulphide reacts has suggested the use of the para-isomeride also.

p-Xylylene hydrosulphide, prepared by adding a boiling alcoholic solution of *p*-xylylene bromide to alcoholic potassium hydrosulphide saturated with hydrogen sulphide (compare Kötz, Abstr., 1900, i, 343), is separated by means of dilute aqueous sodium hydroxide from the simultaneously formed *monoethyl ether* of *p*-xylylene glycol,

$$C_{10}H_{14}O_2,$$

b. p. 250—252°. *p*-Xylylene hydrosulphide condenses, in the presence of hydrogen chloride, with aliphatic aldehydes or ketones to form only amorphous, rather indefinite products, but with aromatic aldehydes beautifully crystalline duplo-compounds are obtained, which are similar to those obtained from pentamethylene hydrosulphide (Autenrieth and Geyer, Abstr., 1909, i, 6). The duplo-compounds contain an eighteen-membered ring, and are very stable; nascent hydrogen does not cause the elimination of hydrogen sulphide or of the mercaptan; oxidising agents do not rupture the ring, and the compounds are stable to boiling alcoholic potassium hydroxide, but

undergo deep-seated changes by treatment with fuming hydrochloric acid at 180°.

Duplo-p-*xylylenebenzylidenemercaptal*,

$$C_6H_4<\begin{matrix}CH_2\cdot S\cdot CHPh\cdot S\cdot CH_2\\CH_2\cdot S\cdot CHPh\cdot S\cdot CH_2\end{matrix}>C_6H_4,$$

m. p. 248—249°, is prepared by passing hydrogen chloride into an ice-cold mixture of equal molecular quantities of benzaldehyde and *p*-xylylene hydrosulphide. It crystallises in silvery leaflets, and has a molecular weight in naphthalene corresponding with its formula. In warm benzene it is oxidised by potassium permanganate and sulphuric acid to the *tetrasulphone*,

$$C_6H_4<\begin{matrix}CH_2\cdot SO_2\cdot CHPh\cdot SO_2\cdot CH_2\\CH_2\cdot SO_2\cdot CHPh\cdot SO_2\cdot CH_2\end{matrix}>C_6H_4,$$

which melts above 300°.

Duplo-p-*xylylene*-p-*tolylidenemercaptal*, $C_{32}H_{32}S_4$, m. p. 266°, is prepared in a similar way, and yields a *tetrasulphone*, $C_{32}H_{32}O_8S_4$, m. p. 280—282° (decomp.). *Duplo*-p-*xylylene*-m-*tolylidenemercaptal*, $C_{32}H_{32}S_4$, m. p. 219—220°, is similarly obtained in almost theoretical yield. *Duplo*-p-*xylylene*-p-*hydroxybenzylidenemercaptal*, $C_{30}H_{28}O_2S_4$, m. p. 262—264° (decomp.), is prepared in ethereal solution, and yields a *dibenzoate*, m. p. 233°, by the Schotten-Baumann process.

Duplo-p-*xylylene*-m-*hydroxybenzylidenemercaptal*, $C_{30}H_{28}O_2S_4$, m. p. 251—252° (decomp.), is also prepared in ethereal solution, and forms a *dibenzoate*, m. p. 169°.

p-Xylylene hydrosulphide forms a *dibenzoate*, m. p. 135°, and a *dibenzyl thioether*, $C_6H_4(CH_2\cdot S\cdot C_7H_7)_2$, m. p. 65°. The latter in benzene solution is oxidised by potassium permanganate and sulphuric acid mainly to the corresponding *disulphone*, $C_{22}H_{22}O_4S_2$, m. p. 292—294° (decomp.); the accompanying *disulphoxide*, $C_6H_4(CH_2\cdot SO\cdot C_7H_7)_2$, m. p. 232—233°, is removed by acetone; it is more conveniently prepared by the addition of 30% hydrogen peroxide to a cold solution of the dibenzyl thioether in glacial acetic acid. C. S.

Poly-membered Heterocyclic Sytems containing Sulphur, and Ring Closure in the Meta-Position. WILHELM AUTENRIETH and FRITZ BEUTTEL (*Ber.*, 1909, **42**, 4357—4361).—The following compounds are prepared by methods similar to those described in the preceding abstract.

m-Xylylene hydrosulphide forms a *dibenzoyl* derivative, $C_6H_4(CH_2\cdot SBz)_2$, m. p. 52·5°, and a *dibenzyl thioether*, m. p. 48°. m-*Xylylenedibenzyldisulphone*, $C_6H_4(CH_2\cdot SO_2\cdot C_7H_7)_2$, has m. p. 225°.

After many attempts with various aliphatic and aromatic aldehydes and ketones, the authors have succeeded in condensing *m*-xylylene hydrosulphide and acetone in the presence of hydrogen chloride, the crystalline product being the *duplo*-m-*xylenemercaptal* of *acetone*, $C_6H_4<\begin{matrix}CH_2\cdot S\cdot CMe_2\cdot S\cdot CH_2\\CH_2\cdot S\cdot CMe_2\cdot S\cdot CH_2\end{matrix}>C_6H_4$, m. p. 254°, which is stable to alcoholic potassium hydroxide, nascent hydrogen, potassium perman-

ganate and sulphuric acid, and hydrogen peroxide; the corresponding *tetrasulphone*, $C_{22}H_{28}O_8S_4$, melts above 300°, and is insoluble in all known organic solvents. Its molecular weight is assumed, by analogy, to correspond with the preceding formula. C. S.

Crystalline Alkaloid of Calycanthus Glaucus. III. *iso*-Calycanthine, Isomeric with Calycanthine. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1909, **31**, 1305—1312).—In earlier papers (Abstr., 1905, i, 295; 1906, i, 35), calycanthine and its salts have been described.

On extracting the alkaloid from a new quantity of seed, a product was obtained which, although resembling calycanthine in composition and general appearance, differs from it in several important respects, and is therefore termed *iso*calycanthine. Whether the two samples of seed were derived from different species of *Calycanthus* or the difference between the alkaloids was due to a difference in the age of the plants is not at present known.

iso*Calycanthine*, $C_{11}H_{14}N_2,\frac{1}{2}H_2O$, m. p. 212—214°, forms crystals of the bisphenoidal class of the orthorhombic system [$a:b:c=1{\cdot}2557:1:1{\cdot}3226$], and has $[\alpha]_D$ 697·97°; the anhydrous alkaloid has m. p. 235—236°. The *hydrochloride, hydrobromide, hydriodide, platinichloride, aurichloride, nitrate, sulphate, hydrogen sulphate, picrate*, and *picrolonate* are described.

The *nitrosoamine*, $C_{11}H_{13}N_2{\cdot}NO$, darkens at 99° and melts at 106—107°. When the alkaloid is left with acetyl chloride for a few weeks, a steel-blue hydrochloride is produced, whilst if the mixture is heated for six hours in a sealed tube, a dark brown hydrochloride is formed. When treated with methyl iodide, the base is converted into its hydriodide, together with two other compounds which have not yet been investigated. If the alkaloid is digested with concentrated sulphuric acid, a product is obtained which is probably a sulphonic acid. E. G.

A New Highly Fluorescent Substance Derived from Physostigmine [Eserine]. PAUL GAUBERT (*Compt. rend.*, 1909, **149**, 852—853).—When an aqueous solution of eserine is kept for several months, it acquires a deep blue tint, and on the addition of phthalic acid develops a red fluorescence which exceeds in intensity that of all known substances. The compound to which this is due has been isolated as dark blue crystals. W. O. W.

Constitution of Stachydrine. ERNST SCHULZE and G. TRIER (*Ber.*, 1909, **42**, 4654—4659. Compare Abstr., 1909, i, 323).—The constitution of stachydrine as the methylbetaine of hygric acid (dimethylbetaine of α-proline) is proved by its conversion into derivatives of hygric acid (Willstätter and Ettlinger, Abstr., 1903, i, 363) and its synthesis from this acid.

The *ethyl* ester of stachydrine hydrochloride forms a syrup, and yields a sparingly soluble *aurichloride*, $C_9H_{18}O_2NAuCl_4$, m. p. 59—60°. When distilled, the hydrochloride of the ester gives a 20% yield of ethyl hygrate, b. p. 77—79°/18 mm.

Stachydrine has been synthesised by converting ethyl hygrate

(ethyl 1-methylpyrrolidine-2-carboxylate) into its methiodide (Willstätter and Ettlinger, *loc. cit.*, 364), and then treating this with silver oxide.

Stachydrine platinichloride, $2C_7H_{13}O_2N,H_2PtCl_6$, crystallises in long, yellow needles. J. J. S.

Synthesis of Indolenine Ketones. GIUSEPPE PLANCHER and D. GIUMELLI (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 393—397).—3 : 3-Dimethylindolenine-2-carboxylonitrile, $C_6H_4<\substack{N\\CMe_2}>C\cdot CN$, previously described as a liquid (Abstr., 1899, i, 543), has been obtained in the solid state, m. p. about 38°.

3 : 3-*Dimethylindolenyl* 2-*methyl ketone*, $C_6H_4<\substack{N\\CMe_2}>C\cdot COMe$, prepared by the action of magnesium methyl iodide on the preceding compound, forms volatile needles, m. p. 130°, is readily resinified by acids, and gives the iodoform reaction with iodine and alkali. With hydroxylamine it gives the oxime, m. p. 175—176°, formed by the action of nitrous acid on 3 : 3-dimethyl-2-ethylindolenine (compare Abstr., 1903, i, 433). The corresponding *semicarbazone*, $C_{13}H_{16}ON_4$, forms scales, m. p. 242°.

The action of magnesium phenyl bromide on 3 : 3-dimethylindolenine-2-carboxylonitrile yields, not a ketone, but the *imino*-compound, $C_6H_4<\substack{N\\CMe_2}>C\cdot CPh\colon NH$, m. p. 103·5°. This imino-derivative is the first intermediate compound formed in Blaise's reaction (Abstr., 1901, i, 133), which proceeds according to the equations: (1) $R\cdot CN + MgR_1Br = CRR_1\colon NMgBr$; (2) $CRR_1\colon NMgBr + H_2O = CRR_1\colon NH + MgBr\cdot OH$, and (3) $CRR_1\colon NH + H_2O = R\cdot CO\cdot R_1 + NH_3$. The above imino-compound does not readily give phase (3) of the reaction, but the imino-group present reacts easily with ketone reagents; thus, the compound gives an *oxime*, $C_{17}H_{16}ON_2$, which forms prisms, m. p. 205°, and a p-*nitrophenylhydrazone*, m. p. 209°.

T. H. P.

Catalytic Hydrogenation of Aromatic and Quinoline Bases. GEORGES DARZENS (*Compt. rend.*, 1909, **149**, 1001—1004. Compare Padoa, Abstr., 1906, i, 765 ; Ipatieff, Abstr., 1908, i, 332).—1 : 2 : 3 : 4-Tetrahydroquinoline is formed when quinoline is hydrogenated at 160—180° in presence of nickel which has been obtained by reduction of its hydroxide at 250—255°. The product is free from indolé and from more highly hydrogenated quinolines. 6-Methyltetrahydroquinoline has been obtained in the same way.

The reduction products of dimethyl- and diethyl-aniline have been investigated by Senderens (Abstr., 1904, i, 660), but have been obtained by the present author in a state of greater purity. *cyclo*-Hexyldimethylamine has b. p. 159°, and forms a *picrate*, m. p. 176—177° ; the corresponding diethyl derivative has b. p. 191°, and forms a *picrate*, m. p. 91—92°.

Attention is drawn to the influence of the temperature at which the nickel is prepared on its behaviour as a catalyst. W. O. W.

Bz-Sulphoquinolinecarboxylic Acids. ALBERT EDINGER and L. BÜHLER (*Ber.*, 1909, **42**, 4313—4320).—In connexion with their work on *Bz*-quinoline mercaptans (Abstr., 1908, i, 363) the authors have prepared the following substances.

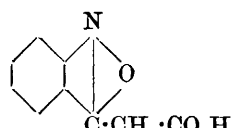
5-*Sulphoquinoline*-8-*carboxylic acid*, $CO_2H\cdot C_9NH_5\cdot SO_3H$, is obtained by oxidising 8-methylquinoline-5-sulphonic acid (Herzfeld, Abstr., 1884, 1198) by chromic and sulphuric acids, and is separated from the unchanged material by crystallisation from dilute sulphuric acid, D 1·16, at 75°; the *copper* and the *barium* salts are mentioned.

6-Methylquinoline-7-sulphonic acid has been prepared by the Skraup reaction, but is obtained in good yield by working under the author's conditions. When heated at 260—270° with a mixture of equal parts of potassium and sodium hydroxides and a little water, it yields 7-*hydroxy*-6-*methylquinoline*, m. p. 244°, b. p. 240°/22 mm., whilst by distilling its sodium salt with potassium cyanide, 7-*cyano*-6-*methylquinoline*, m. p. 133°, is obtained. 7-*Sulphoquinoline*-6-*carboxylic acid* is obtained from 6-methylquinoline-7-sulphonic acid by oxidation with chromic and sulphuric acids; it crystallises in white octahedra, and the *strontium* and *barium* salts are mentioned. By fusion with equal parts of potassium and sodium hydroxides at 275°, a *dihydroxyquinoline*, darkening at 280° and m. p. 321°, is obtained, which crystallises in large, yellow needles, and contains its hydroxyl groups in positions 6 and 7, assuming that intramolecular change has not occurred during the fusion with the alkalis.

8-*Sulphoquinoline*-6-*carboxylic acid* and 6-*sulphoquinoline*-8-*carboxylic acid* are obtained from the corresponding toluquinolinesulphonic acids by processes of oxidation similar to the preceding.

The reaction between sodium 6-sulphoquinoline-8-carboxylate and phosphorus pentachloride at 125—135° yields the sulphonyl chloride, which is reduced by stannous chloride and hydrochloric acid; the resulting tin double salt is decomposed by sodium hydroxide, yielding the corresponding mercaptide, which is converted by the Schotten-Baumann process into the *benzoyl* derivative, m. p. 213°, of quinoline-6-mercaptan-8-carboxylic acid. C. S.

Reduction of o-Nitrophenylpropiolic Acid. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1909, **43**, 4555—4566).—On reduction of *o*-nitrophenylpropiolic acid, indigotin and *o*-aminophenylpropiolic acid have been obtained. When reduction is carried out with zinc dust in ammoniacal solution, a ring compound, *homoanthroxanic acid* (annexed formula), is formed. This crystallises in lustrous, flat needles with a faint yellow shimmer; m. p. 108°. It is a strong carboxylic acid; the alcoholic-aqueous solution reddens litmus; it dissolves in presence of sodium and barium carbonates and sodium acetate. The *silver* salt contains one atom of metal. It is not easily esterified or acetylated, reduces ammoniacal silver and Fehling's solutions on boiling, and gives no coloration with ferric chloride.



When heated at 110—120° it is converted into methylanthroxane, $C_6H_4<\begin{matrix}N\text{——}\\ |\\ CMe\end{matrix}>O$. Sodium nitrite converts it into the *oxime* of anthroxanaldehyde, $\begin{matrix}N\text{——}O\\ | \diagdown |\\ C_6H_4\cdot C\cdot CH:N\cdot OH\end{matrix}$, crystallising in colourless needles, m. p. 172—173°, which can also be prepared from anthroxanaldehyde and hydroxylamine.

On reduction, homoanthroxanic acid at first forms *o*-aminobenzoylacetic acid, which immediately condenses to the anhydride, 4-ketohydrocarbostyril, $C_6H_4<\begin{matrix}N{=}C\cdot OH\\ |\\ CO\cdot CH_2\end{matrix}$, which crystallises in bunches of colourless, hexagonal plates, and is identical with the 4-hydroxycarbostyril described by Baeyer and Bloem (Abstr., 1883, 196); the benzoyl derivative forms radially-grouped, colourless needles, m. p. 220°.

Homoanthroxanic acid, when warmed with hydrochloric acid, is converted into 2 : 3-*dihydroxy*-4-*quinolone*, $C_6H_4<\begin{matrix}NH\cdot C\cdot OH\\ \|\\ CO-C\cdot OH\end{matrix}$ or $C_6H_4<\begin{matrix}N{=}C\cdot OH\\ |\\ CO\cdot CH\cdot OH\end{matrix}$, which forms long, colourless needles, m. p. 276° (decomp.), and gives a characteristic, stable, violet coloration with ferric chloride. The *benzoyl* derivative crystallises in colourless, matted needles, m. p. 216—217° (decomp.). On treatment with phosphorus pentachloride, two crystalline products are obtained: needles, m. p. 85°, volatile in steam, and non-volatile needles, m. p. 205—220°. It is converted into 4-ketohydrocarbostyril on reduction.

E. F. A.

Condensation of α-Diketones with Aldehydes and Primary Arylamines. WALTHER BORSCHE and J. CAMPER TITSINGH (*Ber.*, 1909, 42, 4283—4287. Compare Abstr., 1909, i, 955).—When α-diketones are allowed to react with aldehydes and arylamines under conditions similar to those used in the preparation of cinchonic acids from pyruvic acid, aldol condensation occurs (in one case 2 molecules of the aldehyde reacting with one of the ketone), and the resulting product forms an anil with the arylamine. Thus aniline, benzaldehyde, and acetylbenzoyl (Abstr., 1907, i, 326) react in hot alcoholic solution, yielding *αγ-dihydroxy-αγ-diphenyl-β-phenylglyoxylpropanedianil*, $NPh:CPh\cdot C(:NPh)\cdot CH(CHPh\cdot OH)_2$, which crystallises from glacial acetic acid in yellow needles, m. p. 176° (decomp.). When heated with acetic anhydride and anhydrous sodium acetate, the anil yields an *acetyl* derivative, $C_{37}H_{30}O_2N_2$, probably

$$NPh:CPh\cdot C(:NPh)\cdot C(:CHPh)\cdot CHPh\cdot OAc,$$

which crystallises in colourless needles, m. p. 273°.

When salicylaldehyde is substituted for benzaldehyde in the above condensation, a resin is formed, but with anisaldehyde, *δ-phenyl-α-anisyl-Δ^{α}-butene-γδ-dianil*, $NPh:CPh\cdot C(:NPh)\cdot CH:CH\cdot C_6H_4\cdot OCH_3$, is formed, crystallising in needles, m. p. 153°.

m-Nitrobenzaldehyde yields a similar *anil*,

NPh:CPh·C(:NPh)·CH:CH·C_6H_4·NO_2,

in the form of yellow needles, m. p. 181°.

a-Phenyl-δ-anisyl-Δ^a-butene-γδ-dianil,

OMe·C_6H_4·C(:NPh)·C(:NPh)·CH:CHPh,

obtained from aniline, benzaldehyde, and acetyl-*p*-anisoyl, forms colourless needles, m. p. 203°. When *p*-anisidine is substituted for aniline, the p-*anisil*,

OMe·C_6H_4·C(:N·C_6H_4·OMe)·C(:N·C_6H_4·OMe)·CH:CHPh,

is obtained as yellow needles, m. p. 158°.

Dicinnamoyldianil, CHPh:CH·C(:NPh)·C(:NPh)·CH:CHPh, obtained from diacetyl, benzaldehyde, and aniline in glacial acetic acid solution, forms a yellow, crystalline powder, m. p. 270°.

Acetylbenzoyl, benzaldehyde, and *m*-nitroaniline do not condense.

J. J. S.

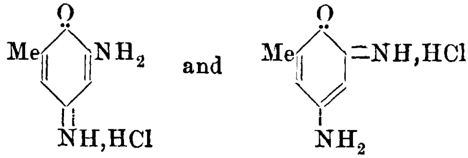
Auxochromic Action of Amino- and Aminophenyl Groups. JEAN PICCARD (*Ber.*, 1909, **42**, 4332—4341).—The intense colour of Wurster's salts and of many dyes, particularly of the triphenylmethane series, is attributed by Willstätter and Piccard (Abstr., 1908, i, 475) to the *meri*-quinonoid constitution of such substances. This view is contraverted by Kehrmann (Abstr., 1908, i, 699), who maintains, in consequence of the behaviour of the aminobenzoquinoneimines (Abstr., 1906, i, 967), that the intense colour is due to the influence of a quinonoid benzene nucleus increased by an auxochromic amino-group. The author shows that by oxidising 3 : 5-diamino-*o*-cresol dihydrochloride in a freezing mixture by an excess of ferric chloride, and adding a saturated solution of potassium nitrate, a light red *holo*-quinonoid *amino*-o-*toluquinoneimine nitrate*, $C_7H_9O_4N_3$, is obtained, which does not show any resemblance to true red dyes in its behaviour in light. When the oxidation is performed with a deficiency of ferric chloride, a dark red *meri*-quinonoid compound is obtained. Also, in solution, Kehrmann's red compounds (*loc. cit.*) differ essentially from red dyes; the latter exhibit pronounced selective absorption, whilst the former show no trace of a band.

Coloured quinonoid substances are classified in two groups: (1) Colour is due to a quinonoid nucleus and an auxochromic amino-group; (2) colour is due to the junction of quinonoid and hydroquinonoid nuclei (*meri*-quinonoid compounds). The preceding light red nitrate is typical of group (1), Wurster's red salt of group (2).

The difference in the colour of triphenylmethaneimine bases and their salts is attributed by Kehrmann to a change in the constitution of the chromophore. From the spectroscopic examination of magenta, the author considers that the triphenylmethane dyes are *meri*-quinonoid compounds belonging to group (2). Substances which contain only an auxochromic amino-group in addition to the quinonoid nucleus are not dyes.

When an aqueous solution of diaminocresol dihydrochloride is oxidised by an excess of ferric chloride in the presence of saturated sodium chloride, a light red aminotoluquinoneimine hydrochloride crystallises at − 15°, and a dark red isomeride at the ordinary

temperature. The former is regarded as the *p*-quinonoid and the latter as the *o*-quinonoid form respectively:



C. S

A Reaction of Polybasic Acids and a New Reaction for Titanium. JEAN PICCARD (*Ber.*, 1909, **42**, 4341—4345).—It is well known that the reduction of organic substances by titanous chloride is accelerated by the addition of potassium sodium tartrate. The author finds that indigotin, Wurster's red, and, in particular, aminotoluquinoneimine hydrochloride (preceding abstract) are very slowly affected by titanous chloride in aqueous or dilute hydrochloric acid solution, but the addition of certain acids, such as tartaric acid, increases the rate of reduction enormously. An examination of about fifty inorganic and organic acids reveals the fact that, in general, polybasic acids exert an accelerative influence, but not so monobasic acids. The most marked effect is produced by hydrofluoric acid (an argument in favour of the polymerised state, H_2F_2), oxalic, glycollic, lactic, pyruvic, tartaric, malic, and citric acids, catechol, and pyrogallol. The remaining halogen acids, and formic, acetic, propionic, butyric, benzoic, β-naphthoic, and monochloroacetic acids have no influence.

Catechol produces with a solution of titanous chloride a yellowish-orange coloration, which is much more intense than that produced by oxalic acid. The test, which is fifteen times more sensitive than the hydrogen peroxide test, should be performed with an excess of catechol and in the absence of mineral acids, and preferably also of alkali hydroxides and carbonates and ammonium hydroxide.

The author suggests that Fenton's brown substance, obtained from dihydroxymaleic acid and compounds of quadrivalent titanium (Trans., 1908, **93**, 1064), may contain tervalent titanium. C. S.

Diketodialkylpiperazines. KARL W. ROSENMUND (*Ber.*, 1909, **42**, 4470—4481).—The author has prepared a number of diketodialkylpiperazines in order to investigate the hypnotic action of the alkyl groups, more especially of the ethyl group, in them. 2 : 5-Diketo-6 : 6-diethylpiperazine exhibits no such action, although, like veronal, it contains two ethyl groups combined with a quaternary carbon atom occurring in a physiologically indifferent ring-system.

α-Bromo-α-ethylbutyric acid (compare Kalle & Co., Abstr., 1907, i, 276) forms white scales, m. p. 20°, b. p. 130—133°/18 mm., and may be prepared in almost theoretical yield by the action of bromine on α-ethylbutyric acid in a sealed tube at 136—140°. Its *ethyl* ester is a colourless liquid, b. p. 87—88°/18 mm. (impure), with an intense camphor-like odour.

α-Amino-α-ethylbutyric acid (compare Gulewitsch and Wasmus, Abstr., 1906, i, 409) is best prepared by the action of methyl-alcoholic

ammonia on α-bromo-α-ethylbutyric acid, its preparation from diethyl ketone by Zelinsky and Stadnikoff's method (Abstr., 1906, i, 425) being difficult and infertile. Its *ethyl* ester, $NH_2\cdot CEt_2\cdot CO_2Et$, is a colourless oil, b. p. 76—77°/15 mm.

a-Chloroacetylamino-a-methylbutyric acid,

$$CH_2Cl\cdot CO\cdot NH\cdot CMeEt\cdot CO_2H,$$

prepared by the action of chloroacetyl chloride and sodium hydroxide on α-amino-α-methylbutyric acid, forms colourless needles, m. p. 162°.

a-Glycylamino-a-methylbutyric acid, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CMeEt\cdot CO_2H$, prepared by the action of aqueous ammonia on α-chloroacetylamino-α-methylbutyric acid, forms white needles, m. p. 245° (decomp.).

3 : 6-*Diketo-2-methyl-2-ethylpiperazine*, $CMeEt{<}{\scriptstyle CO\cdot NH \atop \scriptstyle NH\cdot CO}{>}CH_2$, prepared by the action of ammonia either on a methyl-alcoholic solution of ethyl α-glycylamino-α-methylbutyrate at 0°, or on ethyl α-chloroacetylamino-α-methylbutyrate at 100°, forms slender, white needles, m. p. 250°.

3 : 6-*Diketo-2 : 5-dimethyl-2 : 5-diethylpiperazine*,

$$CMeEt{<}{\scriptstyle CO\cdot NH \atop \scriptstyle NH\cdot CO}{>}CMeEt,$$

prepared by heating ethyl α-amino-α-methylbutyrate in a sealed ube at 240—250°, forms slender needles, subliming on heating, and having m. p. 336° in a closed capillary tube.

a-Chloroacetylamino-a-ethylbutyric acid, $CH_2Cl\cdot CO\cdot NH\cdot CEt_2\cdot CO_2H$, forms small needles or prisms, m. p. 190°.

a-Glycylamino-a-ethylbutyric acid, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CEt_2\cdot CO_2H$, forms white crystals, m. p. 269° (decomp.).

3 : 6-*Diketo-2 : 2-diethylpiperazine*, $CEt_2{<}{\scriptstyle CO\cdot NH \atop \scriptstyle NH\cdot CO}{>}CH_2$, prepared by the action of methyl-alcoholic ammonia at 105° on ethyl α-chloroacetylamino-α-ethylbutyrate, forms long, shining needles, m. p. 272°, having an extremely bitter taste.

Ethyl a-glycylamino-a-ethylbutyrate, m. p. 202—210°, when heated with alcoholic ammonia at 100°, yields only the corresponding free acid, m. p. 269°. This result is not in accord with Fischer's views on the mechanism of the formation of the anhydrides of amino-acids from the esters of halogen-acylamino-acids by the action of ammonia, since, according to these views, the dipeptide esters are formed as intermediate products and give the anhydrides by loss of alcohol. It seems, on the contrary, that the alkoxy-group is first replaced by an amino-group, the amide thus formed losing hydrogen chloride and giving the anhydride :

$$CH_2Cl\cdot CO\cdot NH\cdot CEt_2\cdot CO_2R \longrightarrow CH_2Cl\cdot CO\cdot NH\cdot CEt_2\cdot CO\cdot NH_2 \longrightarrow CEt_2{<}{\scriptstyle CO\cdot NH \atop \scriptstyle NH\cdot CO}{>}CH_2.$$

That such an intermediate amide can be formed is shown by the action of ammonia on the ethyl ester of bromodiethylacetylglycine (*vide infra*).

Ethyl bromoethylbutyrylaminoacetate, $CEt_2Br\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, prepared by the action of bromoethylbutyryl chloride on ethylaminoacetate, has m. p. 35—36°

Bromoethylbutyrylglycinamide, $CEt_2Br\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, obtained by the action of methyl-alcoholic ammonia on the preceding ester, has m. p. 109—110°. This compound exhibits little inclination to ring-closure, and on heating for several hours with methyl-alcoholic ammonia at 100—105°, it yields (1) two isomeric compounds, m. p. 122° and 87—88°, which are apparently the two stereoisomeric α-ethylcrotonylglycinamides, $CHMe\colon CEt\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$ (compare Mannich and Zernik, Abstr., 1908, i, 399), and (2) small quantities of two compounds, m. p. 99—100° and 110° respectively. With pyridine in place of ammonia, a similar reaction occurs.

T. H. P.

Pyrimidines. XLVIII. Synthesis of 5-Cyanouracil. TREAT B. JOHNSON (*Amer. Chem. J.*, 1909, **42**, 505—515).—The work described in this paper was undertaken for the purpose of preparing certain pyrimidines to be used for the synthesis of new thymine derivatives. It has been shown by Wheeler, Johnson, and Johns (Abstr., 1907, i, 559) that ethyl ethoxymethylenemalonate condenses with ψ-thiocarbamides with formation of esters of 2-alkylthiol-6-pyrimidone-5-carboxylic acids, which are readily hydrolysed by hydrochloric acid with production of uracil-5-carboxylic acid. It therefore seemed probable that 5-cyanouracil could be obtained in an analogous manner from ethyl cyanoethoxymethyleneacetate. Experiments have been carried out which show that ethyl-ψ-thiocarbamide condenses with this ester in presence of alkali hydroxide with formation of 5-cyano-2-ethylthiol-6-pyrimidone, together with smaller quantities of ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate (Wheeler and Johns, Abstr., 1907, i, 1083). On hydrolysing the former product with sulphuric acid, a quantitative yield of 5-cyanouracil is obtained.

On adding ethyl cyanoethoxymethyleneacetate (1 mol.) to an alcoholic solution of ethyl-ψ-thiocarbamide (1 mol.), *ethyl α-cyano-β-ethyl-ψ-thiocarbamidoacrylate*, $NH_2\cdot C(SEt)\colon N\cdot CH\colon C(CN)\cdot CO_2Et$, m. p. 130° (decomp.), separates in yellow crystals, and, when warmed with alkali hydroxide, is converted into *5-cyano-2-ethylthiol-6-pyrimidone*, $NH{<}{\begin{smallmatrix}C(SEt)=N\\CO\cdot C(CN)\end{smallmatrix}}{>}CH$, m. p. 222°, which crystallises in prisms. If ethyl cyanoethoxymethyleneacetate (1 mol.) is added to an alcoholic solution of ethyl-ψ-thiocarbamide (1·7 mols.), *α-cyano-β-ethyl-ψ-carbamidoacrylethyl-ψ-thiocarbamide*,

$$NH_2\cdot C(SEt)\colon N\cdot CH\colon C(CN)\cdot CO\cdot N\colon C(SEt)\cdot NH_2,$$

m. p. 164—165° (decomp.), is produced, which crystallises in prisms; this compound is converted by warm sodium hydroxide into 5-cyano-2-ethylthiol-6-pyrimidone and by concentrated hydrochloric acid into 5-cyanouracil.

5-Cyanouracil (2 : *6-diketo-5-cyanopyrimidine*),

$$NH{<}{\begin{smallmatrix}CO\text{——}NH\\CO\cdot C(CN)\end{smallmatrix}}{>}CH,$$

m. p. 295° (decomp.), crystallises in prisms, and by the action of concentrated hydrochloric acid is converted quantitatively into uracil.

When 5-cyano-2-ethylthiol-6-pyrimidone is dissolved in concentrated

hydrochloric acid and the solution evaporated to dryness at 100° 5-cyanouracil is produced, together with *uracil-5-carboxylamide*,

$$NH<\begin{matrix}CO\text{———}NH\\ CO\cdot C(CO\cdot NH_2)\end{matrix}>CH,$$

which forms small prisms, does not melt below 300°, and is converted quantitatively into uracil by concentrated hydrochloric acid. E. G.

Influence of Constitution on the Conversion of Phenylhydrazones of Unsaturated Compounds into Pyrazolines. KARL AUWERS and H. VOSS (*Ber.*, 1909, **42**, 4411—4427).—The method recently described for converting into pyrazolines the phenylhydrazones of unsaturated aldehydes and ketones of the type

$$R\cdot CH{:}CH\cdot CO\cdot R'$$

(Abstr., 1909, i, 59) is now employed to determine how far the readiness to undergo this change is affected by the constitution of the groups R and R′. This paper deals with the aromatic unsaturated aldehydes and ketones. The phenylhydrazone of phenyl styryl ketone changes into 1 : 3 : 5-triphenylpyrazoline even at low temperatures, and cannot be isolated; the phenylhydrazones of cinnamaldehyde and styryl methyl ketone, however, only form pyrazolines at a high temperature. The phenylhydrazones of the following ketones are stable: styryl ethyl ketone, styryl *n*-propyl ketone, styryl *n*-butyl ketone, styryl *n*-nonyl ketone; those of styryl *iso*propyl ketone and styryl *tert.*-butyl ketone are unstable, especially the latter. Hence the structure of the group R′, rather than its weight, seems of importance.

The introduction of an hydroxyl or methoxy-group into the ortho-position in one of the benzene nuclei favours the formation of pyrazolines. From *o*-hydroxystyryl ethyl and propyl ketones only the pyrazolines can be obtained. *o*-Methoxystyryl ethyl ketone and phenylhydrazine also yield a pyrazoline directly. The introduction of a nitro-group has the opposite effect: phenyl *m*- and *p*-nitrostyryl ketones yield phenylhydrazones which are converted into pyrazolines only on boiling with glacial acetic acid. The *p*-nitrophenylhydrazone of cinnamaldehyde cannot be converted into a pyrazoline even by means of this reagent. Furfurylideneacetone behaves like styryl methyl ketone. Cinnamylideneacetophenone yields a stable phenylhydrazone.

For distinguishing between phenylhydrazones and pyrazolines, Knorr's reaction is not to be depended on in every case; reduction with sodium amalgam is a safer criterion; under this treatment all phenylhydrazones yield aniline. *Cinnamaldehyde*-p-*bromophenylhydrazone* forms yellow needles, m. p. 139—140°; when boiled with glacial acetic acid it yields 5-*phenyl*-1-p-*bromophenylpyrazoline*, which crystallises in yellow needles, m. p. 140°. 1 : 5-Diphenyl-3-methylpyrazoline (from styryl methyl ketone) has m. p. 115—116° (Knorr gave 109°: Abstr., 1885, 555). Styryl ethyl ketone-phenylhydrazone has m. p. 104—105° (Harries and Müller gave 101°: Abstr., 1902, i, 295).

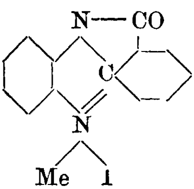
1 : 5-*Diphenyl*-3 : 4 *dimethylpyrazoline*, prepared from a methyl styryl

ethyl ketone-phenylhydrazone, has m. p. 82—83°. *Styryl* iso*propyl ketone* has b. p. 147°/11 mm.; the 1 : 5-*diphenyl*-3-iso*propylpyrazoline* obtained from it forms white needles, m. p. 88·5°. *Styryl* n-*butyl ketone* has b. p. 159—167°/11 mm., and m. p. 38—39°; the *phenylhydrazone* has m. p. 97·5—98·5°. 1 : 5-*Diphenyl*-3-tert.-*butyl pyrazoline* (from styryl *tert.*-butyl ketone) has m. p. 108—108·5°. *Styryl* n-*nonyl ketone-phenylhydrazone* crystallises in silky, felted needles, m. p. 76—77°; when heated with glacial acetic acid it gives a *pyrazoline* in brown crystals, m. p. 60°. *o*-Hydroxystyryl ethyl ketone has m. p. 118—119° (Decker and von Fellenberg, Abstr., 1909, i, 116, give 101°); with phenylhydrazine, it yields directly 1-*phenyl*-5-o *hydroxyphenyl*-3-*ethylpyrazoline*, which crystallises in small needles, m. p. 134°. The substance of m. p. 119°, which Harries and Busse (Abstr, 1896, i, 301) obtained from *o*-hydroxystyryl *n*-propyl ketone, is not, as they assumed, the phenylhydrazone, but 1-*phenyl*-5-o-*hydroxyphenyl*-3-*propylpyrazoline*. When heated with glacial acetic acid it yields a *compound*, m. p. 98—99°, which does not give the pyrazoline reaction. The supposed phenylhydrazone, obtained by the same authors (*loc. cit.*) from phenyl-*o*-hydroxystyryl ketone, is 1 : 3-*diphenyl*-5-o-*hydroxyphenylpyrazoline*; it yields a *mono-benzoyl* derivative, m. p. 172°. o-*Methoxystyryl ethyl ketone*, a yellow oil, gives 1-*phenyl*-5-o-*methoxyphenyl*-3-*methylpyrazoline*, which forms yellow needles, m. p. 87—88°. p-*Nitrostyryl methyl ketone-phenylhydrazone* forms red crystals, m. p. 195—196°; when heated with glacial acetic acid, it yields 1-*phenyl*-5-p-*nitrophenyl*-3-*methylpyrazoline*, which crystallises in small, golden-yellow needles, m. p. 112—113°. *Phenyl*-m-*nitrostyryl ketone-phenylhydrazone* has m. p. 101—103°; boiling glacial acetic acid converts it into 1 : 3-*diphenyl*-5-m-*nitrophenylpyrazoline*, which forms brownish-yellow needles, m. p. 122—123°. *Phenyl* p-*nitrostyryl ketone-phenylhydrazone* crystallises in felted, red needles, m. p. 138—139°; it yields 1 : 3-*diphenyl*-5-p-*nitrophenylpyrazoline*, which forms brownish-yellow needles, m. p. 113—114°. Furfurylideneacetone has b. p. 112—115°/10 mm.; its *phenylhydrazone* forms yellow needles, m. p. 131—132°; 1-*phenyl*-5-*furyl*-3-*methylpyrazoline* crystallises in large, white needles, which are volatile in steam, and have m. p. 102—103°. Cinnamylideneacetophenonephenylhydrazone has m. p. 156—158° (Sorge, Abstr., 1902, i, 379, gave 125—126°). R. V. S.

Benzoylenebenziminazole. HANS RUPE and K. G. THIESS [and, in part, with ALEX. WETTER] (*Ber.*, 1909, **42**, 4287—4304).—*o*-Benzoylenebenziminazole (Thiele and Falk, Abstr., 1906, i, 751) can be prepared by reducing *o*-nitrophthalanil with stannous chloride and hydrochloric acid, or, better (75% of theory), with iron and acetic acid. It crystallises in long, yellow needles with a silky lustre, m. p. 212—213°, and is readily hydrolysed by acids or alkalis to phenylbenziminazole-*o*-carboxylic [benziminazole-2-benzoic] acid, m. p. 266° (Thiele and Falk, 273°). The *hydrochloride* of the acid forms long, lustrous needles. The *methyl ester*, $C_{15}H_{12}O_2N_2$, crystallises in glistening, colourless needles, m. p. 188°. The *aurichloride* of the ethyl ester, $C_{16}H_{15}O_2N_2,AuCl_4$, forms slender, orange-yellow needles, m. p. 120°. When the ethyl ester is

heated, it yields alcohol and the iminazole. The *phenylhydrazide* of the acid, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{N}>C\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, crystallises in colourless needles, m. p. 244°.

Benzoylenebenziminazole methiodide (annexed formula), obtained by heating the iminazole with excess of methyl iodide in sealed tubes at 90—100°, crystallises in slender, bright red needles, m. p. about 200°. When carefully heated above its m. p., it yields methyl iodide and the benziminazole, and when boiled with water yields *benziminazole-2-benzoic acid methiodide*, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{N(MeI)}>C\cdot C_6H_4\cdot CO_2H$, which crystallises in glistening, yellow cubes, m. p. 200—210°.



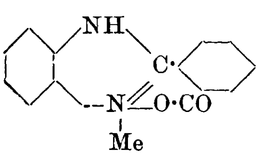
The *methiodide* of the methyl ester, $C_{16}H_{15}O_2N_2I$, is obtained by the action of methyl alcohol on the red methiodide at 90—100°. The *methiodide* of *methyl* 1-*methylbenziminazole*-2-*benzoate*,

$$C_6H_4<\genfrac{}{}{0pt}{}{NMe}{N(MeI)}>C\cdot C_6H_4\cdot CO_2Me,$$

obtained (*a*) by heating benzoylenebenziminazole with excess of methyl iodide and a little methyl alcohol at 120°, (*b*) by heating the methyl ester of the acid with methyl iodide (2 mols.) and a little methyl alcohol at 100°, or (*c*) by heating the methiodide of the methyl ester with methyl iodide at 100°, crystallises in large, compact prisms, m. p. 230°.

The *methiodide* of the ethyl ester, $C_{17}H_{17}O_2N_2I$, forms compact prisms, m. p. 191°. The *methiodide* of *ethyl* 1-*methylbenziminazole*-2-*benzoate*, $C_{18}H_{19}O_2N_2I$, crystallises in colourless needles or long prisms, m. p. 175°.

When heated with ammonium hydroxide solution or with sodium acetate solution at the ordinary temperature, the methiodide of the 2-benzoic acid yields the *betaine* (annexed formula), which crystallises in minute needles, m. p. 280—281°. Its constitution as a betaine is based on the following properties: it dissolves readily in alkali carbonate solutions, and the addition of hydrochloric acid precipitates the methochloride of benziminazole-2-benzoic acid. When heated with acetic anhydride and hydriodic acid, it yields the red methiodide of benzoylenebenziminazole. When heated for some time at 280—290°, it yields benzoylenebenziminazole, methyl alcohol, and unaltered substance.



The *methochloride* of benziminazole-2-benzoic acid, $C_{15}H_{13}O_2N_2Cl$, crystallises in colourless needles, m. p. 272—274°, and with acetic anhydride yields *benzoylenebenziminazole methochloride*, $C_{15}H_{11}ON_2Cl$, greenish-yellow needles, m. p. 200°. The *methobromide* of the acid, $C_{15}H_{13}O_2N_2Br$, has m. p. about 270°, and the *methobromide* of the benzoylenebenziminazole forms yellow needles, m. p. about 230°. When the methiodide of methyl 1-methylbenziminazole-2-benzoate is shaken with moist silver oxide, the corresponding *ammonium* base, $C_{17}H_{18}O_3N_2$, is obtained as a white solid, m. p. 252°.

When benzoylenebenziminazole is covered with nitric acid (D 1·52) and acetic anhydride is added, drop by drop, at 0°, a *nitro*-derivative, I, $C_{14}H_7O_3N_3$, which crystallises in pale yellowish-green needles, m. p. 239°, is formed, together with *nitrobenziminazole*-2-*benzoic acid*, $C_{14}H_9O_4N_3$, colourless needles, m. p. 280—300° (decomp.).

An isomeride, *nitrobenzoylenebenziminazole*, II, is formed when nitric acid (D 1·25) is added to a solution of the iminazole in acetic anhydride; it crystallises in small, brown needles, m. p. 280° (decomp.), and is accompanied by a nitrobenziminazole-2-benzoic acid, which crystallises in orange-coloured needles, m. p. 280—300° (decomp.). This second nitro-acid is a powerful dye.

Aminobenzoylenebenziminazole, I, $C_{14}H_9ON_3$, obtained by reducing the nitro-compound, I, with sodium hyposulphite, crystallises in brilliant red, flat needles, m. p. 298—305°. Its *acetyl* derivative, $C_{16}H_{11}O_2N_3$, forms yellow needles, decomposing at 253°. The base is a dye, and when diazotised and coupled with phenols yields valuable azo-dyes.

o-*Nitrophthalanil*, $NO_2·C_6H_4·N⁚C_2O_2⁚C_6H_4$, obtained by condensing *o*-nitroaniline and phthalic anhydride with sodium acetate, crystallises in pale yellow needles, m. p. 203°. It is stable towards acids, but is readily decomposed by alkalis, and when reduced with a concentrated sodium hyposulphite solution yields o-*aminophthalanil*, $NH_2·C_6H_4·N⁚C_2O_2⁚C_6H_4$, which crystallises in brilliant yellow needles, m. p. 188—189°. The *acetyl* derivative, $C_{16}H_{12}O_3N_2$, forms colourless needles, m. p. 202°; the *hydrochloride*, glistening, colourless needles. When diazotised and coupled with resorcinol, the base yields an *azo-dye*, $C_{20}H_{13}O_4N_3$, as golden-brown plates, m. p. 190°. J. J. S.

Indigotin. II. Indigotin Diarylimides. EUGÈNE GRANDMOUGIN and ED. DESSOULAVY (*Ber.*, 1909, **42**, 4401—4407. Compare Abstr., 1909, i, 968).—*Indigotindianilide hydrochloride*, prepared by the interaction of indigotindianilide in acetic acid with alcoholic hydrogen chloride, forms dark bluish-green needles. The corresponding *sulphate* is very similar.

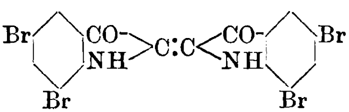
Dehydroindigotindianilide nitrate is prepared by adding four times its weight of 50% nitric acid to indigotindianilide, which immediately changes its blue colour to a brilliant red. The nitrate crystallises in rosettes of red needles; the alcoholic solution is turned violet by alcoholic potassium hydroxide, but on heating it turns a dirty green and indigotindianilide separates. To obtain the corresponding base, the nitrate is suspended in pyridine and oxidised with lead peroxide, whereby a brownish-red, crystalline substance is obtained, which yields red salts with acids and is partly converted on heating into indigotindianilide. The nitrate is a tetranitrate, but part of the nitric acid is lost during drying.

Dehydroindigotindi-p-*toluidide tetranitrate* resembles the anilide, and gives the characteristic violet coloration with potassium hydroxide. The corresponding *tetrahydrochloride* forms a red, crystalline precipitate.

7 : 7′-Dimethylindigotindi-*p*-toluidide, prepared by heating dimethyl-

indigotin with *p*-toluidine and boric acid, crystallises in dark blue needles with a copper reflex. Chromic acid oxidises it to *o*-methylisatin, and nitric acid to the red 7 : 7′-dimethyldehydroindigotindi-*p*-toluidide tetranitrate. E. F. A.

Indigotin. III. 5 : 7 : 5′ : 7′-Tetrabromoindigotin. EUGÈNE GRANDMOUGIN (*Ber.*, 1909, **42**, 4408—4411).—Tetrabromoindigotin is best prepared by brominating indigotin with 8 atoms of bromine in boiling nitrobenzene; it crystallises in lustrous copper crystals. The solubility depends largely on the purity of the product; it forms a blue solution in concentrated sulphuric acid. On oxidation in the cold with nitric acid, 5 : 7-dibromoisatin is formed; distillation with potassium hydroxide gives rise to 2 : 4-dibromoaniline. The constitution is therefore established (annexed formula).



On successive bromination of indigotin, 5 : 5′-dibromo-, 5 : 7 : 5′-tribromo-, and 5 : 7 : 5′ : 7′-tetrabromo-derivatives are formed; on further bromination the halogen probably enters the positions 4 : 4′.

The leuco-compound of tetrabromoindigotin is readily obtained on reduction in alcoholic suspension with sodium hydrogen sulphite. This dissolves in alkalis with a yellow coloration, and dyes cotton yarn fast blue shades. E. F. A.

Preparation of Azines from Nitroso-β-naphthols and *o*-Phenylenediamine. FRITZ ULLMANN and ROBERT HEISLER (*Ber.*, 1909, **42**, 4263—4268).—α-Nitroso-β-naphthol, reacting as the tautomeric naphthaquinoneoxime, condenses with a boiling acetic acid solution of *o*-phenylenediamine in the presence of dilute hydrochloric acid, yielding αβ-naphthaphenazine (Witt, Abstr., 1887, 591):

$$C_{10}H_6{<}{}^{N\cdot OH}_{O} \quad {}^{NH_2}_{NH_2}{>}C_6H_4 + HCl =$$

$$C_{10}H_6{<}{}^{N}_{N}{>}C_6H_4 + 2H_2O + NH_2\cdot OH,HCl,$$

which can be isolated by fractional precipitation with water. It is crystalline, and has m. p. 142°. A by-product formed during the reaction is 2 : 3-diaminophenazine (Griess, *J. pr. Chem.*, 1871, [ii], **3**, 142; Fischer and Hepp, Abstr., 1889, 499).

9-Hydroxynaphthaphenazine (Kehrmann and Brunnel, Abstr., 1908, i, 579) can be obtained from 7-hydroxy-β-naphthaquinoneoxime (Clausius, Abstr., 1890, 627) and *o*-phenylenediamine, or even better from the zinc salt of the nitrosonaphthol. Its *acetyl* derivative, $C_{18}H_{12}O_2N_2$, crystallises in brownish-yellow needles, m. p. 207°. The *methyl ether*, $C_{17}H_{12}ON_2$, forms glistening, yellowish-brown needles, m. p. 168°, and yields solutions with a green fluorescence.

Naphthaphenazine-5-carboxylic acid, $C_{16}N_2H_9\cdot CO_2H$, obtained from 1-nitroso-2 : 3-hydroxynaphthoic acid (Kostanecki, Abstr., 1894, i, 91) and *o*-phenylenediamine, forms yellow needles, and when heated forms αβ-naphthaphenazine. The *sodium* salt, $C_{17}H_9O_2N_2Na$, forms yellow, glistening needles. *Naphthaphenazine-8-sulphonic acid*,

$C_{16}H_{10}O_3N_2S$, obtained from 1-nitroso-2-naphthol-8-sulphonic acid (Meldola, Trans., 1880, **39**, 41) and *o*-phenylenediamine, crystallises in orange-yellow needles. The *barium* salt, $Ba(C_{16}H_9O_3N_2S)_2$, forms a red precipitate.

7-*Acetylamino-naphthaphenazine*, $C_{16}N_2H_9\cdot NHAc$, from 1-nitroso-5-acetylamino-2-naphthol and *o*-phenylenediamine without the aid of hydrochloric acid, crystallises in pale yellow, felted needles, m. p. 311—313°, and when hydrolysed with sulphuric acid yields 7-*amino-naphthaphenazine*, $C_{16}H_{11}N_3$, as glistening, reddish-brown needles, m. p. 270—271°. J. J. S.

Function of the Nitrogen Atoms in Primary Hydrazines. MAX BUSCH (*Ber.*, 1909, **42**, 4596—4602).—A continuation of the investigations of the author and his co-workers on the interaction of primary hydrazines with carbimides and thiocarbimides (compare Abstr., 1901, i, 234; 1903, i, 537; 1904, i, 628). It has been shown (*loc. cit.*) that $\beta\delta$-dialkylthiosemicarbazides are formed by the interaction of hydrazines and thiocarbimides in cold alcohol, whereas $\alpha\delta$-dialkylthiosemicarbazides are produced at higher temperatures or when the components are allowed to interact in the absence of a solvent; it would appear therefore that the amine in cold alcohol is present as an ammonium base, $NHR\cdot NH_3\cdot OH$, in consequence of which it does not form a $\beta\delta$-dialkylthiosemicarbazide, owing to the saturated character of the β-nitrogen atom. This view is supported by the following observations: (1) $\beta\delta$-Diphenylthiosemicarbazide is formed by the interaction of phenylhydrazine and phenylthiocarbimide in alcohol, even at a high temperature, provided an acid, such as acetic or hydrochloric, is present. (2) The product of the reaction when the components are dissolved in benzene or ether, even at a low temperature, contains about 70% of $\alpha\delta$-diphenylthiosemicarbazide.

Phenylcarbimide behaves like its sulphur analogue, but exhibits a greater tendency to combine with the β-nitrogen atom of the hydrazine.

The course of the reaction in the case of alphylhydrazines is not altered by the presence of an acid; thus, methylhydrazine sulphate and benzylhydrazine hydrochloride react with phenylthiocarbimide in alcoholic-acetic acid solution, yielding $\beta\delta$-dialkylthiosemicarbazides.

$\beta\delta$-*Diphenylthiosemicarbazide hydrochloride*, $C_{13}H_{13}N_3S,HCl$, crystallises in small aggregates of microscopic leaflets, softens at 160°, m. p. 170° (decomp.). W. H. G.

Addition of Thiocarbimides to Ring-substituted Arylhydrazines. MAX BUSCH and JOHANNES REINHARDT (*Ber.*, 1909, **42**, 4602—4610).—Contrary to the statement of Marckwald (Abstr., 1897, i, 503), arylhydrazines containing substituents in the ortho-, meta-, or para-positions combine with thiocarbimides in alcoholic solution, particularly in the presence of acetic acid at a low temperature yielding $\beta\delta$-dialkylthiosemicarbazides, which are fairly stable, passing into the $\alpha\delta$-dialkyl isomerides when fused; in a few cases the $\beta\delta$-derivatives have not been isolated owing to experimental difficulties.

δ-*Phenyl*-β-m-*tolylthiosemicarbazide*, $C_{14}H_{15}N_3S$, prepared from

m-tolylhydrazine and phenylthiocarbimide, crystallises in silvery, flat needles or leaflets, m. p. 132—133°, and condenses with benzaldehyde, yielding *δ-phenyl-β-*m*-tolyl-α-benzylidenethiosemicarbazide,*

$$NHPh\cdot CS\cdot N(C_7H_7)\cdot N:CHPh,$$

which crystallises in small, yellow nodules, m. p. 104°. The parent substance remains unchanged when treated with an alcoholic solution of hydrochloric acid, but passes into *δ-phenyl-α-*m*-tolylthiosemicarbazide,* $C_{14}H_{15}N_3S$, glistening, white leaflets, m. p. 156—157°, when heated for a short time at 135°.

δ-o-*Tolyl-β-*m*-tolylthiosemicarbazide* crystallises in colourless leaflets, m. p. 120—121°; the *hydrochloride,* $C_{15}H_{17}N_3S,HCl$, forms white needles, m. p. 162°; δ-o-*tolyl-α-*m*-tolylthiosemicarbazide* forms granular aggregates of microscopic leaflets, m. p. 148°.

δ-p-*Tolyl-β-*m*-tolylthiosemicarbazide* forms glistening leaflets, m. p. 130—131°; the α-m-*nitrobenzylidene* derivative, $C_{22}H_{20}O_2N_4S$, crystallises in pale yellow needles or prisms, m. p. 198°; δ-p-*tolyl-α-*m*-tolylthiosemicarbazide* forms tufts of needles or rectangular prisms, m. p. 145—146°.

Methylthiocarbimide reacts with *m*-tolylhydrazine in the presence of glacial acetic acid, yielding a *substance,* crystallising in glistening, yellow prisms, m. p. 119—120°; an alcoholic solution of the components at 60° yields small quantities of a *substance,* crystallising in white prisms, m. p. 163°.

*δ-Phenyl-β-*m*-chlorophenylthiosemicarbazide* forms small, colourless, compact crystals, m. p. 117°; the *α-benzylidene* derivative,

$$C_{20}H_{16}N_3ClS,$$

crystallises in glistening, white leaflets or hexagonal plates, m. p. 146°; δ-phenyl-α-*m*-chlorophenylthiosemicarbazide has m. p. 153° (slight decomp.); Marckwald gives m. p. 138—139° (*loc. cit.*).

*β-*m*-Chlorophenyl-δ-methylthiosemicarbazide* crystallises in glistening, white needles, m. p. 105°; the α-m-*nitrobenzylidene* derivative,

$$C_{15}H_{13}O_2N_4ClS,$$

forms pale yellow needles, m. p. 224°; *α-*m*-chlorophenyl-δ-methylthiosemicarbazide* has m. p. 177°.

*δ-Phenyl-β-*m*-bromophenylthiosemicarbazide* forms colourless crystals, m. p. 130°; the *benzylidene* derivative, $C_{20}H_{16}N_3BrS$, crystallises in glistening, yellow prisms, m. p. 164°; δ-phenyl-α-*m*-bromophenylthiosemicarbazide has m. p. 159—160°; the compound described by Marckwald (*loc. cit.*), m. p. 113°, is probably a mixture of the isomerides.

α-Bromophenyl-δ-methylthiosemicarbazide has m. p. 175° (decomp.) (Illgen gives m. p. 127—128°: *Diss.*, Berlin, 1894); a *substance* crystallising in tufts of white needles, m. p. 103°, is obtained by the action of methylthiocarbimide on *m*-bromophenylhydrazine in cold alcoholic solution; it is not an α-thiosemicarbazide.

*δ-Phenyl-β-*m*-nitrophenylthiosemicarbazide* forms aggregates of flat, pale yellow needles, m. p. 133°; the *benzylidene* derivative,

$$C_{20}H_{16}O_2N_4S,$$

crystallises in pale yellow, matted needles, m. p. 165—166°.

δ-Phenyl-β-2-naphthylthiosemicarbazide, prepared by acting on β-naphthylhydrazine with phenylthiocarbimide in alcohol containing

acetic acid, crystallises in leaflets, m. p. 185°; the corresponding δ-*methyl* compound forms leaflets, m. p. 172° (decomp.); the *benzylidene* derivative of the former substance, $C_{24}H_{19}N_3S$, forms white leaflets, m. p. 206—207°.

δ-*Phenyl-β-o-tolylthiosemicarbazide* crystallises in glistening, white leaflets, m. p. 124°.

δ-*Phenyl-β-o-anisylthiosemicarbazide* forms leaflets, m. p. 140—141°; the m-*nitrobenzylidene* derivative, $C_{21}H_{18}O_3N_4S$, crystallises in small, rectangular, yellow plates, m. p. 199—200°. W. H. G.

Isatinanils. I. Isatin-dimethylamino-2-anil. Its Formation, Hydrate, and Salts. RUDOLF PUMMERER and MAX GOETTLER (*Ber.*, 1909, **42**, 4269—4279).—Isatin-2-anils (α-isatinanilides) can be prepared by the condensation of aromatic nitroso-derivatives with indoxylic acid in aqueous alcoholic solution. When nitrosobenzene and indoxylic acid are used, isatin-2-anil, m. p. 125—126°, is obtained.

With *p*-nitrosodimethylaniline and indoxylic acid in neutral or faintly acid solution at 15°, the chief product is a violet, crystalline powder, m. p. 105°, which yields isatin with sulphuric acid. Recrystallisation of the violet compound from 80% acetone converts it into *isatin*-p-*dimethylamino-2-anil*, $C_6H_4{<}{}^{NH}_{CO}{>}C{:}N{\cdot}C_6H_4{\cdot}NMe_2$, which crystallises in intensely coloured prisms with a green, metallic lustre. It contains $1{\cdot}5H_2O$, and has m. p. 182°. When powdered it has a green colour, but gives a red streak. When heated at 100° it loses its water of hydration and forms dichroic prisms with a metallic lustre, and then crystallises in bluish-red prisms, m. p. 182°. When the anil or its hydrate is shaken with an excess of an ethereal solution of hydrogen chloride, a yellow *dihydrochloride*,

$$C_{16}H_{15}ON_3,2HCl,$$

m. p. 135—136°, is obtained, but when an excess of hydrogen chloride is avoided, a *monohydrochloride*, $C_{16}H_{15}ON_3,HCl,0{\cdot}5H_2O$, is formed; it crystallises in brilliant blue prisms with a violet, metallic lustre, and readily absorbs water. When heated to about 120°, an isomeric yellow *monohydrochloride* is formed, and from its deep reddish-brown aqueous solution isatin is gradually precipitated. Rubbing the blue salt with chloroform or acetone also transforms it into the yellow isomeride.

The *oxalate*, $C_{16}H_{15}ON_3,1{\cdot}5H_2C_2O_4$, crystallises in blue needles, m. p. 155°. The *picrate*, $2C_{16}H_{15}ON_3,C_6H_3O_7N_3$, crystallises in bluish-black prisms, m. p. 179—180°.

When alkylated with sodium ethoxide and methyl iodide, the anil gives a *methyl* derivative, $C_{17}H_{17}ON_3$, which crystallises in lustrous, black plates, m. p. 125—126°, and yields 1-methylisatin on hydrolysis with hydrochloric acid.

Acids readily decompose *p*-dimethylamino-2-anil into isatin and *p*-aminodimethylaniline salts, which react in the presence of sodium carbonate, yielding *isatin*-p-*dimethylamino-3-anil*, $C_{16}H_{15}ON_3$, m. p. 221—222°.

Violet-coloured dyes are formed when nitroso-compounds are condensed with indoxylic acid in alkaline solution. J. J. S.

Preparation of 1-*p*-Dialkylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 214716).—The 1-*p*-dialkylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolones are of therapeutic interest as being remarkably powerful antipyretics; they are produced by alkylating 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone with methyl iodide or methyl sulphate, the former methylation taking place in alcoholic solution. 1-p-*Dimethylaminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone* is a colourless, crystalline substance melting at 212—213°. 1-p-*Aminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone*, colourless prisms, m. p. 249°, is produced by reducing 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolene*, yellow crystals, m. p. 178—179°, the latter being obtained by condensing *p*-nitrophenylhydrazine and methyl acetoacetate to 1-*p*-nitrophenyl-3 : 4-dimethyl-5-pyrazolone, methylating this compound to 1-p-*nitrophenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone*, yellow needles, m. p. 132°, brominating to 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*bromomethyl*-5-*pyrazolone*, m. p. 213—214°, then treating this substance with alkali acetate in glacial acetic acid, whereby the bromine is replaced by hydroxyl, yielding 1-p-*nitrophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone acetate*, yellow crystals, m. p. 163—164°, which, on hydrolysis with dilute sulphuric acid, gives the nitro-alcohol.

F. M. G. M.

Preparation of Xanthine and Guanine Derivatives containing Substituents in Position 8. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 213711).—The *o*-diaminopyrimidines, $Y{:}C{<}{\begin{matrix}NX\text{———}CO\\NX\cdot C(NH_2)\end{matrix}}{>}C\cdot NH_2$, yield formyl, acetyl, and propionyl derivatives, which, when heated, undergo further condensation to furnish xanthine and guanine compounds. This reaction has been generalised, with the result that the following acids can be employed for the condensation: oxalic, succinic, cyanoacetic, glycollic, lactic, hydantoic, α-hydroxy*iso*butyric, hippuric, acetylglycollic, ethoxy- and methoxyacetic, and αβ-dihydroxypropionic acids.

4-*Amino*-5-*oxalylamino*-2 : 6-*dioxy*-3-*methylpyrimidine*,

$$CO{<}{\begin{matrix}NH\text{———}CO\\NMe\cdot C(NH_2)\end{matrix}}{>}C\cdot NH\cdot CO\cdot CO_2H,$$

is obtained by condensing, at 160—170°, 4 : 5-diamino-2 : 6-dioxy-3-methylpyrimidine and fused oxalic acid; it crystallises with $1H_2O$, and gives a *disodium* salt, which, on heating at 150—160°, yields the sodium salt of 3-*methylxanthine*-8-*carboxylic acid*,

$$\begin{matrix}NH\text{—}CO\cdot C\cdot NH\\ | \qquad\quad \| \\ CO\cdot NMe\cdot C\text{—}N\end{matrix}{>}C\cdot CO_2H,$$

the free acid of which crystallises with $1\frac{1}{2}H_2O$, and at 160° gives rise to 3-*methylxanthine*.

4-*Amino*-5-*cyanoacetylamino*-2 : 6-*dioxy*-1 : 3-*dimethylpyrimidine*,

$$CO{<}{\begin{matrix}NMe\cdot CO\text{———}\\NMe\cdot C(NH_2)\end{matrix}}{>}C\cdot NH\cdot CO\cdot CH_2\cdot CN,$$

acicular crystals, is obtained by heating, at 120—130°, 4 : 5-diamino-2 : 6-dioxy-1 : 3-dimethylpyrimidine with cyanoacetic acid.

Theophylline-8-acetic acid, $\begin{matrix}\mathrm{NMe\cdot CO\cdot C\cdot NH} \\ \mathrm{CO\cdot NMe\cdot C\!-\!\!-N}\end{matrix}\!\!>\!\mathrm{C\cdot CH_2\cdot CO_2H}$, is produced by heating the foregoing compound with aqueous sodium hydroxide until ammonia is completely evolved; it separates from water in aggregates of white needles.

Ethyl theophylline-8-acetate, prepared by passing hydrogen chloride into the foregoing compound suspended in alcohol, forms crystals, melting at 215°.

2 : 4-*Diamino-5-succinylamino-6-pyrimidone*,

$$\mathrm{NH_2\cdot C}\!\!<\!\!\begin{matrix}\mathrm{N\!:\!C(OH)} \\ \mathrm{N\cdot C(NH_2)}\end{matrix}\!\!>\!\mathrm{C\cdot NH\cdot CO\cdot C_2H_4\cdot CO_2H},$$

prepared from 2 : 4 : 5-triamino-6-pyrimidone and succinic acid, gives rise to *succinylguaninepropionic* acid and the *hydrochloride* of *ethyl guaninepropionate*, $\mathrm{HCl,NH_2\cdot C}\!\!<\!\!\begin{matrix}\mathrm{N\!:\!C(OH)\cdot C\cdot NH} \\ \mathrm{N\!-\!\!-\!\!-\!\!-\!\!-\!\!-C\!-\!\!-N}\end{matrix}\!\!>\!\mathrm{C\cdot C_2H_4\cdot CO_2Et}$.

4-*Amino-5-cyanoacetylamino-2 : 6-dioxy-3-methylpyrimidine*,

$$\mathrm{CO}\!<\!\!\begin{matrix}\mathrm{NH\!-\!\!-\!\!-\!\!-\!\!-CO} \\ \mathrm{NMe\cdot C(NH_2)}\end{matrix}\!\!>\!\mathrm{C\cdot CO\cdot CH_2\cdot CN},$$

prepared from 4 : 5-*diamino*-2 : 6-*dioxy*-3-*methylpyrimidine* and cyanoacetic acid, furnishes 3-*methylxanthine*-8-*acetic acid* on heating with excess of aqueous sodium hydroxide. The *compound*,

$$\mathrm{CO}\!<\!\!\begin{matrix}\mathrm{NMe\cdot CO\cdot C\cdot NH} \\ \mathrm{NMe\!-\!\!-\!\!-\!\!-C\!-\!\!-N}\end{matrix}\!\!>\!\mathrm{CH_2\cdot OH},$$

m. p. 240°, is obtained by heating 4 : 5-diamino-2 : 6-dioxy-1 : 3-dimethylpyrimidine and hydroxyacetic acid, and then warming the first condensation product with concentrated aqueous barium hydroxide.

The patent contains examples of several other condensation products of similar type containing lactyl, succinyl, and aceturyl groups.

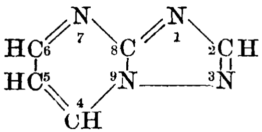
F. M. G. M.

Hydrazo-compounds. IV. Reactions of Hydrazobenzene with Aliphatic Aldehydes and with Benzoyl Chloride. BERTHOLD RASSOW and OTTO BAUMANN (*J. pr. Chem.*, 1909, [ii], 80, 511—518).—The investigations of Rassow and Lummerzheim (Abstr., 1901, i, 777) have been extended to other aldehydes.

1 : 2 : 4 : 5-*Tetraphenyl*-3 : 6-*dihexylhexahydro*-1 : 2 : 4 : 5-*tetrazine*, $\mathrm{C_6H_{13}\cdot CH}\!<\!\!\begin{matrix}\mathrm{NPh\cdot NPh} \\ \mathrm{NPh\cdot NPh}\end{matrix}\!\!>\!\mathrm{CH\cdot C_6H_{13}}$, m. p. 133°, is obtained by adding heptaldehyde to a hot solution of hydrazobenzene in 90% alcohol. Equal molecular quantities of hydrazobenzene and propaldehyde react with development of heat to form mainly *propylidenebishydrazobenzene*, NHPh·NPh·CHEt·NPh·NHPh, m. p. 152°. The minor product of the reaction, 3 : 6-*diethylhexahydro*-1 : 2 : 4 : 5-*tetrazine*, m. p. 193°, becomes the sole product when the aldehyde is added to hot 90% alcoholic hydrazobenzene.

Benzoylhydrazobenzene, NPhBz·NHPh, m. p. 136°, is obtained in 80% yield when an ethereal solution of hydrazobenzene and benzoyl chloride (2 mols.) is boiled with magnesium oxide; a second benzoyl group cannot be introduced. C. S.

Synthetical Experiments on the Preparation of Derivatives of Hetero-condensed-heterocyclic "1 : 3-Triazo-7 : 0′-pyrimidine" [1 : 3 : 7 : 9-Benztetrazole]. CARL BÜLOW and KARL HAAS (*Ber.*, 1909, **42**, 4638—4644).—5-Amino-1 : 3 : 4-triazole (Thiele and Manchot, Abstr., 1899, i, 168) condenses with 1 : 3-diketones in much the same manner as 1-amino-1 : 3 : 4-triazole (Bülow and Weber, Abstr., 1909, i, 614, 615); two molecules of water are eliminated, and derivatives of "1 : 3-triazo-7 : 0′-pyrimidine" [1 : 3 : 7 : 9-benztetrazole] (annexed formula) are formed.



When the 5-aminotriazole is condensed with ethyl acetoacetate and its homologues, 6- or 5 : 6-substituted derivatives of 4-hydroxy-1 : 3 : 7 : 9-benztetrazole (heterohydroxylic acids) are obtained. The presence of the hydroxylic group imparts strongly acidic properties to the compounds, so that they yield neutral sodium salts, and can be titrated readily by means of standard alkali.

4 : 6-*Dimethyl*-1 : 3 : 7 : 9-*benztetrazole*, $\begin{array}{l}\mathrm{CMe{=}N{\cdot}C{:}N} \\ \mathrm{CH{:}CMe{\cdot}N{\cdot}N}\end{array}\!\!>\mathrm{CH}$, obtained by boiling an alcoholic solution of 5-amino-1 : 3 : 4-triazole with acetylacetone and a few drops of piperidine for fifteen hours, crystallises in colourless needles, m. p. 133°. It is readily volatile, it forms an unstable compound with nitric acid, and with silver nitrate an additive compound, $C_7H_8N_4,AgNO_3$, which crystallises in short, stout needles.

4 : 5 : 6-*Trimethyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_8H_{10}N_4$, obtained in a similar manner from methylacetylacetone, crystallises in colourless needles, m. p. 135—136°.

Benzoylacetone condenses slowly with 5-amino-1 : 3 : 4-triazole in glacial acetic acid solution, yielding tarry matter and 6-*phenyl*-4-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_{12}H_{10}N_4$, which crystallises in needles, m. p. 134°.

4-*Hydroxy*-6-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, $\begin{array}{l}\mathrm{CMe{=}N{-}C{:}N} \\ \mathrm{CH{:}C(OH){\cdot}N{\cdot}N}\end{array}\!\!>\mathrm{CH}$, obtained by boiling for two hours a glacial acetic acid solution of 5-amino-1 : 3 : 4-triazole with ethyl acetoacetate, crystallises in colourless, glistening needles, m. p. 271° after sintering at 261°. A solution of the potassium salt gives amorphous precipitates with solutions of silver and copper salts. The *mercuric*, *lead*, *zinc*, *barium*, *calcium*, and *cobalt* salts have been obtained in crystalline forms.

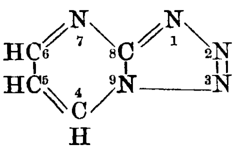
4-*Hydroxy*-6-*methyl*-5-*ethyl*-1 : 3 : 7 : 9-*benztetrazole*, $C_8H_{10}ON_4$, obtained from ethyl ethylacetoacetate and 5-methyl-1 : 3 : 4-triazole, crystallises in felted needles, m. p. 268° after sintering at 250°. Crystalline *copper*, *cadmium*, *manganese*, *calcium*, and *magnesium* salts have been prepared.

When a glacial acetic acid solution of ethyl diacetylsuccinate is boiled for four hours with the 5-aminotriazole, *ethyl* 1-(2′ : 4′ : 5′-)-*triazolyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,

$$\begin{array}{l}\mathrm{CH{\cdot}N} \\ \mathrm{N{-}N}\end{array}\!\!>\mathrm{C{\cdot}N}<\!\!\begin{array}{l}\mathrm{CMe{:}C{\cdot}CO_2Et} \\ \mathrm{CMe{:}C{\cdot}CO_2Et}\end{array}$$

(compare Abstr., 1906, i, 906), is obtained. It crystallises from benzene and has m. p. 113°. J. J. S.

Hetero-condensed, Heterocyclic Compounds with Two Nuclei: Substituted "Tetrazotopyrimidines." CARL BÜLOW (*Ber.*, 1909, **42**, 4429—4438).—*C*-Aminotetrazotic acid reacts with 1 : 3-diketones and with the esters of 1 : 3-ketocarboxylic acids similarly to 1-aminotriazole (Abstr., 1909, i, 614, 615), with production of derivatives of 1 : 2 : 3-tetrazoto-7 : 0′-pyrimidine [1 : 2 : 3 : 7 : 9-benzpentazole] (annexed formula).



Condensation of aminotetrazotic acid with acetylacetone yields 4 : 6-*dimethyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, which crystallises in long needles and has m. p. 150°. From methylacetylacetone, 4 : 5 : 6-*trimethyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, m. p. 123—123·5°, is obtained; it also crystallises in needles. 5-*Phenyl*-6-*methyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, prepared from benzoylacetone, forms white needles, m. p. 185°.

C-Aminotetrazotic acid condenses with ethyl acetoacetate, forming 4-*hydroxy*-6-*methyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, which crystallises in needles, and has m. p. 246—247°; it yields crystalline, *mercurous*, *mercuric*, *lead*, *barium*, *iron*, and *strontium* derivatives. 4-*Hydroxy*-6-*phenyl*-1 : 2 : 3 : 7 : 9-*benzpentazole*, prepared from ethyl benzoylacetate, forms white needles, m. p. 261° (decomp.). Both these compounds are strongly acidic, and may be titrated sharply with phenolphthalein; they are therefore to be regarded as heterohydroxylic acids (Abstr., 1909, i, 615).

By diazotising *C*-aminotetrazotic acid (Thiele, Abstr., 1892, 1299) and treating the product with acetoacetic ester, the azo-compound, *ethyl tetrazolylazoacetoacetate*, $\begin{matrix} N\text{---}N \\ \| \\ N\cdot NH \end{matrix}\!\!>\!C\cdot N\!:\!N\cdot CHAc\cdot CO_2Et$, is obtained; it forms yellow needles, m. p. 140—141°. The *phenylhydrazone* has m. p. 192—193°; on continued boiling with glacial acetic acid, it is converted into 4-*tetrazolylazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, which has m. p. 201° (decomp.), and is apparently dimorphous (orange-yellow needles and deep red, compact crystals). R. V. S.

Preparation of a Soluble Double Compound of Theophylline and Piperazine. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 214376).—*Piperazine-theophylline* is formed by combining molecular proportions of its components; it has an alkaline reaction, and is readily soluble in water, more sparingly so in alcohol. F. M. G. M.

The Gelatinisation of Egg-Albumin by Hydrochloric Acid. I. GIOVANNI MORUZZI (*Biochem. Zeitsch.*, 1909, **22**, 232—243). —The electrical conductivities and depression of freezing points of mixtures of egg-white solution and hydrochloric acid of concentrations $N = 0$ to $N \times 0{\cdot}692$ were determined, and compared with these physical constants for the same strengths in the absence of proteins. The degree of gelatinisation was noted in each case in the mixtures of

protein with acid. The maximum of $\Delta - \Delta'$ was noted when the normality of the acid reached 0·055, and remained about constant until the normality 0·554 was reached. In higher concentrations the value $\Delta - \Delta'$ was negative. The gelatinisation occurred between the concentration 0·103 and 0·244*N*. Experiments were also made to determine the changes of the viscosity of the mixtures during the process of gelatinisation, when the strength of acid = 0·018*N*. The electrical resistance and depression of freezing point remained constant during the time in which the viscosity increased. The change produced is apparently therefore neither molecular nor ionic, but probably due to a hydration of the colloid. S. B. S.

The Hexone Bases from White of Egg. H. G. CHAPMAN and J. M. PETRIE (*J. Physiol.*, 1909, **39**, 341—345).—By complete hydrolysis of 100 grams of egg-white with 25% sulphuric acid, the yield of hexone bases was as follows: arginine, 2·39; histidine, 0·66, and lysine, 3·19 grams. W. D. H.

The Caseinogen-Peptones containing Phosphorus. M. DIETRICH (*Biochem. Zeitsch.*, 1909, **22**, 120—130).—The products investigated were made by the peptic digestion of caseinogen, and isolated by Reh's method by means of precipitation by uranium salts. They were converted into calcium salts, which were separated into two fractions, one of which was insoluble on heating, and the other soluble. The former was dissolved in water, acidified with acetic acid, the solution neutralised, and from the solution thus obtained, other fractions were separated by means of copper, zinc, and lead salts. The fractions differed from one another in their readiness to yield inorganic phosphorus on hydrolysis. From the fractions of calcium salt which did not separate on heating, a peptone was separated by precipitation with uranyl acetate. The uranium precipitate was decomposed by hydroferrocyanic acid. The nitrogen and phosphorus were estimated in the various fractions. The caseinphosphoric acid isolated by means of the zinc salt was obtained in the largest quantity. It yielded, on hydrolysis, lysine, proline, and glutamic acid. S. B. S.

Synthesis through Ferment Action. ALONZO E. TAYLOR (*Zeitsch. physikal. Chem.*, 1909, **69**, 585—597. Compare Abstr., 1909, ii, 344).—General remarks on the reversibility of enzyme reactions. G. S.

Action of Proteolytic Enzymes on Protamines. M. TAKEMURA (*Zeitsch. physiol. Chem.*, 1909, **63**, 201—214).—The following enzymes were found capable of acting on protamines in a weakly acid medium. Hedin's lieno-β-protease, Hahn and Geret's endotryptase, and papain. The action of pepsin is slight, and probably due to admixture with β-proteases. W. D. H.

Reversibility of Enzyme Actions and the Effect of External Factors on Enzymes (Invertase, Maltase). FRIEDRICH G. KOHL (*Bied. Zentr.*, 1909, **38**, 718; from *Beiheft Bot. Centr.*, 1908,

23, i, 646—640).—Yeast extracts which were found to contain the largest amounts of invertase were allowed to act, in absence of light, on sucrose solutions of known strength at fixed temperatures, after excluding bacterial infection by means of thymol or chloroform. It was found that the dextrose and lævulose increased for some time, after which the amounts generally remained stationary or the enzyme action was reversed. The time depended on the concentration and the temperature. Diffused daylight retards inversion, and 0·05% of asparagine quickens the hydrolysis. N. H. J. M.

Hydrolysis of Salicin by the Enzyme Emulsin. C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1909, **31**, 1242—1249).—The hydrolysis of salicin by strong acids has been shown by Noyes and Hall (Abstr., 1896, ii, 159) to follow the law of unimolecular reactions. It has been stated by Henri, however, that the hydrolysis of the glucoside by emulsin does not take place in accordance with this law, and that the dextrose produced has $[\alpha]_D$ 52°.

Experiments have now been carried out which have given the following results. The dextrose formed by the action of emulsin on salicin is β-dextrose, $[\alpha]_D$ 20°. During the hydrolysis, the readings of the polarimeter are affected by the mutarotation of the dextrose, and this constituted a source of error in Henri's determinations. Measurements of the true rate of hydrolysis of salicin by emulsin at 0° and 30° have been made by rendering the solution slightly alkaline before determining its rotatory power. The results show that the rate follows the unimolecular order. Emulsin is only active in a nearly neutral solution, the activity being completely destroyed by sodium hydroxide of 0·005*N* and by hydrochloric acid of 0·014*N* concentration. E. G.

Influence of Acids on the Loss of Activity of Rennet Caused by Shaking. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physikal. Chem.*, 1909, **69**, 547—556).—When a glycerol extract of rennet, diluted with water, is vigorously shaken in a tube, it rapidly loses its activity. The effect does not depend on the dissolving of alkali from glass, as it is also observed in quartz tubes.

In the quantitative experiments, the rennet solution was contained in a tube of Jena glass, and agitated by the up-and-down motion of an ebonite stirrer. The diminution of activity with the time of shaking does not follow any simple law; the rate of the diminution increases rapidly as the temperature is raised, but becomes less as the enzyme concentration is increased.

Acids, even in great dilution, lessen the rate of diminution of activity very considerably. Hydrochloric acid is most efficient in this respect; lactic, oxalic, and tartaric acids are about equally efficient, and acetic acid is least effective. The behaviour of sulphuric acid is remarkable, inasmuch as above a certain concentration further addition of acid has no action.

Commercial preparations of rennet are not affected by shaking, probably because they contain acids and neutral salts. G. S.

Chemical Composition and Biological Function of an Oxydase. HANS EULER and IVAR BOLIN (*Zeitsch. physikal. Chem.*, 1909, **69**, 187—202).—The preparation of an oxydase from *Medicago sativa* is described. The fresh plants were comminuted, the juice pressed out, treated with alcohol, the precipitate redissolved, again precipitated by alcohol, and this process repeated several times. The product, in the form of a white powder, very soluble in water, was again dissolved in water, the solution boiled and filtered to remove proteins, the filtrate treated with charcoal, again filtered, precipitated with three times its volume of 96% alcohol, and the resulting powder dried in a vacuum. The preliminary treatment of the juice with alcohol may be omitted. The product, which showed all the properties of an oxydase, proved on analysis to consist of the neutral salts (mainly calcium salts) of certain polybasic organic acids, among which glycollic, mesoxalic, citric, malic, and probably glyoxylic acids have been detected. The acids were partly separated by fractional crystallisation of their barium salts.

Experiments on the accelerating influence of "laccase" and of salts of organic hydroxy-acids on the oxidation of polyphenols by free oxygen in the presence of manganese salts have already been described (compare Abstr., 1908, ii, 1021), and these experiments have now been extended. The rate of absorption of oxygen increases less rapidly than the manganese concentration, and also less rapidly than the concentration of the neutral salt of the oxyacid employed. The neutral salts of the different acids differ somewhat in catalytic power, but the effect is independent of the nature of the cation.

The physiological action of the oxydases is discussed. They do not effect the direct oxidation of sugars or fats. Sugar is partly broken down under the influence of enzymes, and the simpler compounds thus formed then undergo oxidation. G. S.

Preparation of Derivatives of Phenylarsenious Oxide and of Arsenobenzene. FARBWERKE VORM MEISTER, LUCIUS and BRÜNING (D.R.-P. 212205. Compare Abstr., 1908, i, 591; 1909, i, 347).—*2-Aminotolyl-5-arsenious oxide*, $NH_2\cdot C_6H_3Me\cdot AsO$, a white, crystalline powder, m. p. 160°, is prepared by reducing 4-amino-3-tolylarsinic acid in sulphuric acid solution by means of sulphurous acid in presence of potassium iodide.

Acetylaminocarboxyphenylarsenious oxide, $NHAc\cdot C_6H_3(AsO)\cdot CO_2H$, a colourless powder, is prepared by boiling 2-acetylaminotolyl-5-arsinic acid during two hours with phenylhydrazine in methyl-alcoholic solution.

o-Tolylglycine-5-arsinic acid, $CO_2H\cdot CH_2\cdot NH\cdot C_6H_3Me\cdot AsO(OH)_2$, m. p. 220° (decomp.), is prepared by treating 2-aminotolyl-5-arsinic acid with chloroacetic acid, and on reduction with sodium hyposulphite at 50° yields *p-arseno-*o*-tolylglycine*, a yellowish-brown powder, which blackens when heated above 200°. *Arsenoacetylanthranilic acid*, a bright yellow powder, is prepared by reducing 2-acetylaminotolyl-5-arsinic acid with sodium hyposulphite in the presence of sodium acetate. F. M. G. M.

Organic Chemistry.

Cuprous Compounds of Ethylene and of Carbon Monoxide. WILHELM MANCHOT and W. BRANDT (*Annalen*, 1909, **370**, 286—296). —Manchot and Friend have shown (Abstr., 1908, ii, 375) that the combination of cuprous chloride with carbon monoxide depends on the formation of a compound, $CuCl,CO,2H_2O$, or analogous substances containing ammonia, aniline, toluidine, etc., in place of water. It is now found that cuprous chloride and ethylene likewise combine, forming a dissociative compound in which one mol. of ethylene is united with 1CuCl; the combination takes place, however, only in the presence of water, aniline, etc.; cuprous chloride does not form an additive product with dry ethylene, neither do these substances interact when dissolved in absolute alcohol.

All attempts to isolate the additive compound, which is far more soluble in water than cuprous chloride, have been unsuccessful, owing to the readiness with which it dissociates. Under identical conditions the ethylene compound is dissociated, as a general rule, to a far greater degree than the analogous carbon monoxide compound.

As in the case of the compounds of ferrous salts with nitric oxide (compare Manchot and Zechentmayer, Abstr., 1907, ii, 93), so also with the additive products of cuprous chloride with carbon monoxide and ethylene: when the concentration of the gas is kept constant the degree of dissociation is increased by raising the temperature.

W. H. G.

Specific Gravity of Solutions of Alcohols: Mixtures of Propyl Alcohol with Water. ANTONY G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1428—1438).—The authors first discuss the literature concerning the specific gravity of propyl alcohol and its aqueous solutions. Their own experiments on the carefully purified and dehydrated alcohol give the value D_{15}^{15} 0·80804 and the conductivity $0·089 \times 10^{-6}$ at 15°, these numbers not being altered by further distillation of the alcohol over calcium. The specific gravities of aqueous solutions containing from 0 to 100% of the alcohol were determined, the results being tabulated; the contractions for the various mixtures have been calculated.

T. H. P.

Stereochemical Isomerides of Δ^{γ}-Hexin-$\beta\epsilon$-diol. GEORGES DUPONT (*Compt. rend.*, 1909, **149**, 1381—1383).—*Δ^{γ}-Hexin-$\beta\epsilon$-diol*, OH·CHMe·C⋮C·CHMe·OH, has been described by Iotsitch (*Journ. Russ. Phys. Chem. Soc.*, 1903, **35**, 430). When this compound is treated with bromine in chloroform solution, it yields a *dibromide*, m. p. 214—215°, mentioned by Iotsitch. The liquid from which this crystallises contains an isomeric *dibromide*, $C_6H_{10}O_2Br_2$, m. p. 119—120°. When treated with zinc dust and alcohol, these derivatives

give two isomeric glycols: Iotsitch's compound, yielding crystals, m. p. 69—70°, b. p. 122°/15 mm., D_{13} 1·0205, $n_D^{13°}$ 1·4698, and forming a *diacetyl* derivative, m. p. 36°. The second glycol is a viscous liquid, b. p. 121°/15 mm., D_{13} 1·023, n_D 1·4733; the *diacetyl* derivative has m. p. 23—24°. Both glycols regenerate the corresponding dibromide when treated with bromine.

It follows, therefore, that the glycol prepared by Iotsitch is a mixture of these two isomerides. W. O. W.

Oxidation of Unsaturated Compounds with Organic Superoxides. NIKOLAUS PRILESCHAÉEFF (*Ber.*, 1909, **42**, 4811—4815. Compare Gambarjan, Abstr., 1909, i, 910).—Oxidation was carried out with benzoylhydroperoxide ($C_6H_5 \cdot CO \cdot O \cdot OH$) dissolved in a neutral solvent at 0°, to which the calculated quantity of the unsaturated compound was added. The temperature is not allowed to rise above ordinary room temperature. The following oxides have been characterised.

Octylene oxide has b. p. 157—158°/740 mm., D_0^0 0·8395, D_{15}^{15} 0·8272, n_D^{15} 1·4165. On hydration, a glycol, b. p. 135—136°/20 mm., is obtained.

Diisobutylene oxide has b. p. 138—139°/765·5 mm, D_0^0 0 8418, D_{16}^{16} 0·8290, n_D^{16} 1·4157. It yields two glycols: *methyl*iso*amylethylene glycol*, m. p. 60—61°, and *dimethyl*-tert.-*butylethylene glycol*, m. p. 64·5—65°.

Decylene oxide has b. p. 116—117°/50 mm., D_0^0 0 8465, D_{16}^{16} 0·8337, n_D^{16} 1·4275. The corresponding *glycol* has b. p. 151—152°/14 mm.

Propylene oxide, b. p. 162—163°/751 mm., D_0^0 1·1270, D_{16}^{16} 1·1136, n_D^{16} 1·4350. It does not yield glycerol on hydration, but forms a *hydroxychloroacetate*, b. p. 125—127°/17 mm.

Geraniol oxide has b. p. 157—158°/25 mm., D_0^0 0·9716, D_{16}^{16} 0·961, n_D^{16} 1·4681. A *triol*, b. p. 205—207°/20 mm., is formed on hydration.

Geraniol dioxide, formed when 2 mols. of benzoyl hydroperoxide are employed, has b. p. 180—183°/25 mm., D_0^0 1·0587, D_{16}^{16} 10472, n_D^{16} 1·4653. On hydration, a *trioloxide*, b. p. 220°/15 mm., m. p. 137—138°, is formed.

Linalool oxide has b. p. 95°/25 mm., D_0^0 0 9660, D_{16}^{16} 0·9507, $[\alpha]_D$ − 4·98°, n_D^{16} 1·4554. It yields a doubly unsaturated *aldehyde* when hydrated, b. p. 120—122°/25 mm., D_0^0 0·8706, D_{16}^{16} 0·8573, n_D^{16} 1·5038, of which the *semicarbazone* has b. p. 138·5°.

Linalool dioxide has b. p. 131—133°/25 mm., D_0^0 1·0552, D_{16}^{16} 1·0423, $[\alpha]_D$ +5·34°, n_D^{16} 1·4616. It forms a *trioloxide*, b. p. 210—212°/25 mm., when hydrated.

Citral oxide has b. p. 146—148°/20 mm., D_0^0 1·0091, D_{16}^{16} 0·9740, n_D^{16} 1·4604, and gives a *diolaldehyde*, b. p. 141—142°/24 mm., D_0^0 1·0584, D_{16}^{16} 1·0335, when hydrated.

Citronellal oxide has b. p. 130—131°/25 mm , D_0^0 0·9437, D_{16}^{16} 0·9344, n_D^{16} 1·4421. On hydration, a *diolaldehyde*, b. p. 180—182°/18 mm., is formed.

Limonene oxide has b. p. 113—114°/50 mm., D_0^0 0·9435, D_{16}^{16} 0 9303, $[\alpha]_D$ − 6·76°, n_D^{16} 1·4693, and yields a *glycol*, m. p. 66·5—67·5°.

Limonene dioxide has b. p. 146·5—147°/50 mm., D_0^0 1·0471,

D_{16}^{16} 1·0338, $[\alpha]_D$ +52·23°, n_D^{16} 1·4702. It forms an amorphous erythritol on oxidation, b. p. above 220°/23 mm.

Pinene oxide has b. p. 102—103°/50 mm., D_0^0 0·9812, D_{16}^{16} 0·9689, $[\alpha]_D$ −92°, n_D^{16} 1·4708; it is readily hydrated, forming sobrerol, m. p. 150°.

Aniline and 1 mol. of benzoylhydroperoxide form azobenzene; with 2 mols., nitrosobenzene is formed. In each case, a little nitrobenzene is formed. *o*-Toluidine gives *o*-nitrotoluene. E. F. A.

Results of Heating the Chlorides of the Higher Fatty Acids. AUGUSTIN BISTRZYCKI and AUGUST LANDTWING (*Ber.*, 1909, **42**, 4720—4723).—The chlorides of the higher primary fatty acids do not lose carbon monoxide when heated (compare Abstr., 1908, i, 270), but it is now shown that they lose hydrogen chloride. Palmityl chloride, when heated at 250—275° for four hours in a current of dry carbon dioxide, gives an almost theoretical yield of hydrogen chloride. From the residue a small amount of a product, *tris-tetradecylketen*, $(C_{16}H_{30}O)_3$, has been isolated, which crystallises from alcohol in plates. It softens at 60°, is completely molten at 72°, and is analogous to the compounds obtained by Wedekind and Haeussermann (Abstr., 1908, i, 671) by the action of tertiary amines on acyl chlorides.

Lauryl chloride, under similar conditions, yields a *product*, $C_{12}H_{22}O$, m. p. 49—58°, and nonyl chloride, a solid product. J. J. S.

α-Ethylpentenoic Acids and Xeronic Anhydride. FRITZ FICHTER and HANS OBLADEN (*Ber.*, 1909, **42**, 4703—4707. Compare Fichter and Mueller, Abstr., 1906, i, 622).—*γ-Methyl-α-ethylparaconic acid*, $CO<\begin{matrix}O\text{——}CHMe\\CHEt\cdot CH\cdot CO_2H\end{matrix}$, obtained by reducing α-ethylacetylsuccinic ester with sodium amalgam and alcohol, has b. p. 192—196°/12 mm., and crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 111°. When distilled slowly under atmospheric pressure, it yields unaltered acid, xeronic anhydride (Fittig, *Annalen*, 1887, **188**, 59), and *α-ethyl-Δ^β-pentenoic acid*, $CHMe{:}CH\cdot CHEt\cdot CO_2H$. The latter forms a gummy *barium* salt, has b. p. 116°/12 mm., and when boiled with 20% sodium hydroxide solution yields a mixture of α-ethyl-Δ^α-pentenoic acid and unaltered Δ^β-acid, the latter of which can be removed as α-ethylvalerolactone by treatment with 62% sulphuric acid (Young, Abstr., 1883, 455).

The Δ^α-unsaturated acid has b. p. 120°/12 mm., and its *barium* salt, $(C_7H_{11}O_2)_2Ba,H_2O$, crystallises in slender needles.

γ-Methyl-α-ethylitaconic acid, $CHMe{:}C(CO_2H)\cdot CHEt\cdot CO_2H$, is formed when xeronic anhydride, $O<\begin{matrix}CO\cdot CEt\\CO\cdot CEt\end{matrix}$, is boiled with 20% sodium hydroxide solution for twenty-four hours. The acid forms slender crystals, m. p. 136°, and yields an *anhydride*, $C_8H_{10}O_3$, as an oil, b. p. 142—144°/12 mm.

Xeronic anhydride and *p*-toluidine yield *xeronic*-p-*tolil*, needles, m. p. 107°. The isomeric *γ-methyl-α-ethylitacon*-p-*tolil* has m. p. 88° and b. p. 220°/12 mm. J. J. S.

β-Methylpentenoic Acids. FRITZ FICHTER and ERWIN GISIGER (*Ber.*, 1909, **42**, 4707—4710).—A comparison of the dissociation constants of β-methyl-Δ^{α}-pentenoic acid and β-methyl-Δ^{β}-pentenoic acid shows that the Δ^{β}-unsaturated acid is the stronger acid; the values for K are Δ^{α}-acid, 0·00073, and Δ^{β}-acid, 0·00255 (compare Abstr., 1904, i, 965; 1906, i, 622). The Δ^{β}-acid was prepared by reducing α-methylacetylsuccinic ester (Bischoff, Abstr., 1881, 412) with sodium and aqueous alcohol to βγ-dimethylparaconic acid, and distilling the latter slowly under atmospheric pressure. It was not found possible to isolate the isomeric Δ^{α}-acid from the mixture of acids obtained by boiling the Δ^{β}-acid with 10% sodium hydroxide solution, as both acids are converted by 62% sulphuric acid into β-methylvalerolactone (compare following abstract). The Δ^{α}-acid was therefore prepared by the elimination of hydrogen bromide from α-bromo-β-methyl-β-ethylpropionic acid.

βγ-Dimethylparaconic acid, $CO<\begin{matrix}CH_2\cdot CMe\cdot CO_2H \\ O\text{——}CHMe\end{matrix}$ (50% yield), has b. p. 196°/9 mm., and crystallises in plates, m. p. 80°. The *ethyl* ester has b. p. 134°/10 mm. *β-Methyl-Δ^{β}-pentenoic acid*,

$$CHMe\colon CMe\cdot CH_2\cdot CO_2H,$$

has b. p. 96°/10 mm., or 199° under atmospheric pressure.

Ethyl α-bromo-β-methyl-n-*valerate*, $CH_2Me\cdot CHMe\cdot CHBr\cdot CO_2Et$, obtained by brominating β-methylvaleric acid (Bentley, Trans., 1895, **67**, 264) by Auwers and Bernhardi's method (Abstr., 1891, 1189), using a Hirsch shaking apparatus, and subsequent treatment of the product with ethyl alcohol, has b. p. 91°/12 mm. When heated with quinoline, hydrogen bromide is eliminated and *ethyl β-methyl-Δ^{α}-pentenoate*, $CH_2Me\cdot CMe\colon CH\cdot CO_2Et$, b. p. 176°, is formed. The corresponding *acid*, $C_6H_{10}O_2$, has m. p. 46° and b. p. 104°/12 mm., or 207° under atmospheric pressure. The *calcium* salt, $(C_6H_9O_2)_2Ca,H_2O$, crystallises in brilliant plates, and the *zinc* salt, which also contains $1H_2O$, in needles.

The formation of the isomeric Δ^{β}-unsaturated acid by the removal of hydrogen bromide from the brominated ester was not observed (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). J. J. S.

Remarkable Transformation of β-Dialkylated Acrylic Acids when Boiled with Sulphuric Acid. FRITZ FICHTER, ALBERT KIEFER, and WALTER BERNOULLI (*Ber.*, 1909, **42**, 4710—4713).—Fittig's statement (Abstr., 1894, i, 204) that Δ^{β}-unsaturated acids are transformed into the isomeric lactones when heated with 62% sulphuric acid, whereas the Δ^{α}-unsaturated acids are unaffected, is not without exceptions (compare Blaise and Luttringer, Abstr., 1905, i. 168). It is shown that β-methyl-Δ^{α}-pentenoic acid (preceding abstract) is quantitatively transformed into β-methylvalerolactone when heated with 62% sulphuric ac d. Under similar conditions, β-ethyl-Δ^{α}-pentenoic acid yields β-ethylvalerolactone.

Ethyl iso*pentylmalonate*, $CHEt_2\cdot CH(CO_2Et)_2$, obtained from γ-iodopentane and sodioethylmalonate, has b. p. 130°/16 mm. The *acid*, $C_8H_{14}O_4$, has m. p. 58°, and yields a *sodium hydrogen* salt,

$$C_8H_{13}O_4Na,9H_2O,$$

in the form of colourless plates. *β-Ethyl*-n-*valeric acid*,

$$CHEt_2\cdot CH_2\cdot CO_2H,$$

has b. p. 212°. *Ethyl α-bromo-β-ethyl*-n-*valerate*, $CHEt_2\cdot CHBr\cdot CO_2Et$, has b. p. 165°/25 mm., and with quinoline yields *ethyl β-ethyl-Δ^α-pentenoate*, $CEt_2\text{:}CH\cdot CO_2Et$, which has b. p. 187—188°. The *acid*, $C_8H_{13}O_2Br$, has b. p. 217—218°, and the *toluidide*, $C_{14}H_{19}ON$, has m. p. 95° and b. p. 210—215°/15 mm. J. J. S.

Decomposition of Crotonic Acid by Heating with Ammonia. FRITZ FICHTER and HANS P. LABHARDT (*Ber.*, 1909, **42**, 4714—4715. Compare Engel, Abstr., 1888, 1063).—When crotonic acid is heated with the compound $CaCl_2,8NH_3$ for eight to ten hours at 225—230°, the chief product is 2-methyl-5-ethylpyridine (Auerbach, Abstr., 1893, i, 175). The formation of this compound is to be attributed to the decomposition of the crotonic acid into acetaldehyde and acetic acid, and the condensation of the former to aldehydecollidine.

[With ALBERT KIEFER.]—Dimethylacrylic acid under similar conditions yields *s*-trimethylpyridine. J. J. S.

Synthesis of β-Hydroxy-α-*iso*propylbutyric Acid. I. MATZUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1319—1324).—The action of zinc on a mixture of acetaldehyde and ethyl α-bromo-β-methylbutyrate (α-bromo*iso*valerate) proceeds according to the equations: (1) $CHMe_2\cdot CHBr\cdot CO_2Et + Zn = CHMe_2\cdot CH(ZnBr)\cdot CO_2Et$; (2) $CHMe_2\cdot CH(ZnBr)\cdot CO_2Et + CH_3\cdot CHO =$

$$ZnBr\cdot O\cdot CHMe\cdot CH(CHMe_2)\cdot CO_2Et,$$

and the latter $+ H_2O = OH\cdot CHMe\cdot CHPr^{\beta}\cdot CO_2Et + ZnBr\cdot OH$.

*Ethyl β-hydroxy-α-*iso*propylbutyrate*, $OH\cdot CHMe\cdot CHPr^{\beta}\cdot CO_2Et$, best prepared in presence of benzene, is a yellow, mobile liquid with a faint, pleasant odour, b. p. 111·5—114°/38—37 mm., D_4^{30} 0·97182, n_D^{30} 1·43296; it gives the normal molecular weight in boiling ether. The corresponding *acid* was obtained as an almost colourless liquid; the *sodium*, *potassium*, and *barium* salts were prepared and analysed. T. H. P.

Ketens. XIV. Ethyl Ethylketencarboxylate. HERMANN STAUDINGER and ST. BEREZA (*Ber.*, 1909, **42**, 4908—4918. Compare this vol., i, 46).—An ethereal solution of ethyl bromoethylmalonate chloride reacts with zinc, producing ethyl ethylketencarboxylate,

$$CO\text{:}CEt\cdot CO_2Et,$$

which rapidly polymerises, forming, with 80% yield, 1 : 3-*diethyl*cyclo*butan*-2 : 4-*dione*-1 : 3-*dicarboxylate*, $CO_2Et\cdot CEt<^{CO}_{CO}>CEt\cdot CO_2Et$, which distils in a high vacuum at 113—116° as a colourless oil. With aniline it yields ethyl ethylmalonanilate. When heated in an oil-bath at 180—200°, it is depolymerised, and the unimolecular keten passes over. *Ethyl ethylketencarboxylate* so prepared is a colour-

less liquid, b. p. 48°/15 mm., m. p. 57·86°. It has the characteristic properties, not of a ketoketen, but of an aldoketen. It is probable that all ketens form bimolecular polymerides, which are *cyclo*butane derivatives. The bimolecular polymeride of keten itself is probably not an acetylketen (compare Chick and Wilsmore, Trans., 1908, **93**, 946), but Δ^1-*cyclobuten-1-ol-3-one*, $CO\!<\!\substack{CH_2\\CH}\!\!>\!C\cdot OH$.

Ethyl ethylmalonate chloride, obtained from the ester-acid by means of phosphorus pentachloride, has b. p. 75—77°/13 mm. It yields an *anilide*, m. p. 55—56°. *Ethyl bromoethylmalonate chloride*, prepared from the above chloride by the action of bromine in hot carbon disulphide solution, has b. p. 95—102°/14 mm. R. V. S.

Action of Ethyl Bromoacetate and Zinc on the Anhydrides of Monobasic Acids. ANDREAS LUNIAK (*Ber.*, 1909, **42**, 4808—4811). —By the interaction of molecular quantities of ethyl bromoacetate and acid anhydrides, *C*-diacyl compounds are obtained. Thus acetic anhydride yielded ethyl-α-acetylacetoacetate, isolated as the copper salt, m. p. 149°. From propionic anhydride the *copper* salt of *ethyl dipropionylacetate* was obtained, crystallising in dark violet crystals, which turned greyish-green at 84° (corr.), m. p. 98° to a dark green liquid. *Ethyl dipropionylacetate* is a colourless liquid of characteristic odour, b. p. 120·5—121·5°/20 mm., D_4^{20} 1·0527. The *copper* salt of *ethyl dibutyrylacetate* forms a bright violet precipitate of thin prisms; it becomes greyish-green at 89° (corr.), m. p. 98°. *Ethyl dibutyrylacetate* is a colourless liquid, b. p. 139—140°/24 mm., D_4^{20} 1·0168, and shows a dark red coloration with ferric chloride. *Ethyl O-butyrylbutyrylacetate* (*β-butyryloxy-Δ^α-hexenoate*),

$$CH_2Me\cdot CH_2\cdot C(O\cdot CO\cdot C_3H_7)\!:\!CH\cdot CO_2Et,$$

has a characteristic fruity odour, b. p. 137—137·5°/12 mm., D_4^{20} 0·9956, and shows no ferric chloride coloration. E. F. A.

Action of Magnesium *tert.*-Butyl Chloride on Ethyl Oxalate. Mlle. V. I. EGOROVA (*J. Russ. Phys. Chem., Soc.*, 1909, **41**, 1454—1468). —In syntheses of alcohols by means of organo-magnesium compounds, just as in syntheses effected with organo-zinc derivatives, the reactions may proceed in two directions, according to the conditions. One of these conditions is the temperature, the raising of which promotes reduction, and another, which is not possessed by aromatic radicles, the more or less marked reducing properties of the radicle combined with the magnesium (compare Bouveault, Abstr., 1904, i, 546; Sabatier and Mailhe, Abstr., 1905, i, 706; Letellier, Abstr., 1908, i, 242). With ethyl oxalate and magnesium *tert.*-butyl chloride, as was to be expected, the reaction follows an abnormal course, owing to the pronounced reducing properties of the Grignard compound. In order that both the ethoxy-groups of the ethyl oxalate may react, to 1 mol. of the oxalate must be taken 4 mols. of magnesium *tert.*-butyl chloride, 2 mols. for the introduction of the radicles, and two for forming the 2 mols. of magnesium hydrogen chloride necessary for the reduction.

The reaction gives rise to the following products: (1) *iso*butylene;

(2) α-hydroxy-ββ-dimethylbutyric acid, $CMe_3\cdot CH(OH)\cdot CO_2H$, which forms rectangular plates, m. p. 87—88°; (3) *α-ethoxy-ββ-dimethylbutyric acid*, $CMe_3\cdot CH(OEt)\cdot CO_2H$, m. p. 121°, the *calcium* salt of which is more soluble in cold than in hot water; (4) the ethyl ester of another acid, formed only in small quantity; (5) the *ketone*, $CMe_3\cdot CO\cdot CH_2\cdot CMe_3$, which is a colourless liquid, b. p. 152·5—154·5°, with a camphor-like odour, and is probably formed by the dehydration, by the alcoholic potassium hydroxide employed for hydrolysis, of part of (6) the *glycol*, $CMe_3\cdot CH(OH)\cdot CH(OH)\cdot CMe_3$, m. p. 90—92°, b. p. 120—130°/33 mm., which has a camphor-like odour; (7) hexamethylethane.

The formation of these various products is explained by the following scheme:

(1) $CO_2Et\cdot CO_2Et + CMe_3\cdot MgCl = CMe_3\cdot C(OEt)(OMgCl)\cdot CO_2Et$; (2) $CMe_3\cdot MgCl = CH_2{:}CMe_2 + MgHCl$; (3) $CMe_3\cdot C(OEt)(OMgCl)\cdot CO_2Et + MgHCl$ gives either $CMe_3\cdot CH(OMgCl)\cdot CO_2Et \longrightarrow$
$CMe_3\cdot CH(OH)\cdot CO_2Et \longrightarrow CMe_3\cdot CH(OH)\cdot CO_2H$ or $CMe_3\cdot CH(OEt)\cdot CO_2Et \longrightarrow CMe_3\cdot CH(OEt)\cdot CO_2H$. When, on the other hand, 2 mols. of the organo-magnesium compound take part in the reaction, the latter proceeds as follows: (1) $CO_2Et\cdot CO_2Et + 2CMe_3\cdot MgCl = CMe_3\cdot C(OEt)(OMgCl)\cdot C(OEt)(OMgCl)\cdot CMe_3$, and (2) this $+ 2MgHCl \longrightarrow CMe_3\cdot CH(OMgCl)\cdot CH(OMgCl)\cdot CMe_3 \longrightarrow CMe_3\cdot CH(OH)\cdot CH(OH)\cdot CMe_3$; (3) $CMe_3\cdot CH(OH)\cdot CH(OH)\cdot CMe_3 - H_2O = CMe_3\cdot CO\cdot CH_2\cdot CMe_3$, and (4) $CMe_3\cdot MgCl + CMe_3Cl =$
$CMe_3\cdot CMe_3 + MgCl_2$.

T. H. P.

Production of Traces of Formaldehyde in the Oxidation of Ethyl Alcohol by Chemical, Physical, or Biological Methods. E. Voisenet (*Compt. rend.*, 1910, **150**, 40—43).—Advantage has been taken of the coloration developed by formaldehyde in a solution of albumin containing nitrous acid, to test for this substance in the products of oxidation of pure alcohol (Abstr., 1906, ii, 59). Definite proof of the presence of formaldehyde was obtained whether the oxidation was effected by the chromic acid mixture, by electrolysis, by contact with finely divided metals, or through the agency of micro-organisms. W. O. W.

A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and Other Plants. Philippe Malvezin *Bull. Soc. chim.*, 1909, [iv], **5**, 1096—1098).—When cupric hydroxide, or copper hydrogen carbonate, is suspended in a 40% aqueous solution of formaldehyde, and sulphur dioxide is passed through the mixture, a deep blue solution is formed. This contains the substance represented by the formula: $Cu(SO_3\cdot CH_2\cdot OH)_2$, which it is proposed to call cupric diformaldisulphite. The following is suggested as the method of formation of this product: $CH_2O \longrightarrow CH_2(OH)_2 \longrightarrow OH\cdot CH_2\cdot O\cdot SO_2H \longrightarrow Cu(SO_3\cdot CH_2\cdot OH)_2$. The advantages in practice of this substance as a fungicide over "Bordeaux mixture" and other cupric products are described. T. A. H.

Catalytic Hydrogenation of Unsaturated Organic Compounds. H. FOURNIER (*Bull. Soc. chim.*, 1910, [iv], 7, 23—27).—The substance to be reduced is placed in a flask containing platinum-black, and communicating with a supply of hydrogen. Sometimes it is advantageous to dissolve the substance in ether. The mixture is kept continuously agitated, and the action continued until hydrogen is no longer absorbed. The catalytic activity of the platinum may be restored when necessary by heating the metal for a few minutes at 200—220°.

Under these conditions crotonaldehyde furnishes *n*-butyraldehyde and *n*-butyl alcohol, *iso*safrole and safrole give dihydrosafrole, and eugenol and *iso*eugenol yield dihydroeugenol [propylguaiacol] (compare Delange, *Bull. Soc. chim.*, 1908, [iv], 3, 505, and Parrain, Abstr., 1907, i, 43). T. A. H.

Conversion of *iso*Butyl Alcohol into α-Methylglyceraldehyde. SIMON ZEISEL and M. DANIEK (*Monatsh*, 1909, 30, 727—728. Compare Viguier, Abstr., 1909, i, 691).—*iso*Butyl alcohol was converted into *iso*butaldehyde, and this by means of bromine in presence of marble transformed into the *methylacetal* of *α-bromo*iso*butaldehyde.* Potassium hydroxide at high temperatures converted this into the *methylacetal* of α-methylacraldehyde, from which, by means of potassium permanganate, α-methylglyceraldehyde methylacetal was obtained and converted into the free aldehyde. E. F. A.

Preparation and Description of Condensation Products of Sodium Derivatives of the Acyloins (Hydroxyketones) with Esters of the Acetic Series. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1909, [iv], 5, 1136—1144).—An extension of a paper already published (Abstr., 1907, i, 479), giving details of the methods of preparation used, descriptions of compounds prepared by the general reaction, and in some cases additional data regarding substances described already. It is now proposed to represent the condensation products of this reaction by the following typical formula:

$$\begin{array}{l} CH_2R\cdot CH\cdot CH_2 \\ CHR{:}C\text{——}O \end{array}\!\!>CO,$$

whilst the esters from them are to be represented by that formerly proposed (*loc. cit.*):

$$\begin{array}{l} CH_2R\cdot CH \\ CH_2R\cdot C{=} \end{array}\!\!>C\cdot CO_2Me.$$

The reasons for the adoption of these formulæ are as follows. The condensation products are (1) only feebly acid, (2) form dibromides, and (3) are readily attacked by oxidising agents, giving 1 mol. each of a fatty acid and a substituted succinic anhydride, (4) the esters formed from them are reduced by sodium in alcohol to homologues of *cyclo*propanecarbinol, so that they must contain a trimethylene ring and a double linking in the αβ-position with respect to the carboxyl group.

The condensation products were prepared as already described (*loc. cit.*). They gave small yields of esters when esterified by the usual methods, and recourse was therefore had to the use of

diazomethane for this purpose. In this way yields of about 80% of the theoretical were obtained.

The product $\begin{matrix} CHEt\cdot CH\cdot CH_2 \\ CHMe:C\text{———}O \end{matrix}\!\!>\!CO$, b. p. 190—195°/12 mm., obtained from propioin, is liquid at the ordinary temperature, and cannot be obtained crystalline (*loc. cit.*).

The corresponding *substance*, $C_{10}H_{16}O_2$, b. p. 210—215°/20 mm., m. p. 116°, obtained from butyroin, crystallises from boiling water; it furnishes an *amide*, m. p. 63—64°, and yields an *ethyl* ester, $C_{12}H_{20}O_2$, b. p. 160°/18 mm. (approx.), and a *methyl* ester, b. p. 143—148°/10 mm. The latter on reduction furnishes *dipropyl*cyclo*propanecarbinol*, b. p. 96—98°/8 mm. or 104—105°/12 mm., which has a mint-like odour, and yields an *acetate* having the same boiling point as itself, and a *pyruvate*, b. p. 125°/8 mm. (approx.), of which the *semicarbazone* has m. p. 97—98°.

*iso*Butyroin under the same conditions yields a *product*, $C_{10}H_{16}O_2$, b. p. 200—210°/25 mm., which crystallises in part.

Hexonoin yields a substance, $C_{14}H_{24}O_2$, b. p. 250—260°/20 mm. and m. p. 100—111° (*loc. cit.*), which on keeping decomposes spontaneously, yielding valeric acid and a second acid, possibly amylsuccinic acid. The methyl ester from this condensation product has b. p. 205°/19 mm. (*loc. cit.*). T. A. H.

Effect of Negative Substituents on the Formation of Semicarbazones. HANS RUPE and SIDONIUS KESSLER (*Ber.*, 1909, **42**, 4715—4720. Compare this vol., i, 15).—The influence of negative groupings (Rupe and Metz, Abstr., 1903, i, 535) on semicarbazone formation is shown in the following reactions. β-Bromo*iso*butyl methyl ketone, $CMe_2Br\cdot CH_2\cdot COMe$, forms a semicarbazone readily, mesityl oxide dibromide, $CMe_2Br\cdot CHBr\cdot COMe$, with difficulty, and bromomesityl oxide, $CMe_2:CBr\cdot COMe$, does not form a semicarbazone.

Aliphatic oximino-ketones react with semicarbazide, yielding semicarbazones, and with excess of the carbazide the oximino-group is eliminated and bis-semicarbazones are formed. Oximino-derivatives of the aromatic series react but slowly with semicarbazide, or, in some cases, do not react at all.

*Methyl β-bromo*iso*butyl ketone*, $C_6H_{11}OBr$, obtained by the addition of hydrogen bromide to mesityl oxide, is a clear, colourless oil, b. p. 52—53°/11 mm., and when kept, even in the absence of air, forms a dark-coloured syrup. The *semicarbazone*,

$$CMe_2Br\cdot CH_2\cdot CMe:N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in slender, colourless needles, m. p. 113° (decomp.).

Mesityl oxide dibromide (Claisen, this Journ., 1876, i, 985), obtained by passing a current of carbon dioxide saturated with bromine vapour into mesityl oxide cooled with ether and solid carbon dioxide, yields a *semicarbazone*, $C_7H_{13}ON_3Br_2$, which crystallises in pale yellow, glistening needles, m. p. 290—295°.

Oximinoacetone-semicarbazone, $OH\cdot N:CH\cdot CMe:N\cdot HN\cdot CO\cdot NH_2$, forms small, colourless, pointed needles, m. p. 218° (decomp.), and yields an *acetyl* derivative, $C_6H_{10}O_3N_4$.

Oximinomethyl propyl ketone-semicarbazone,

OH·N:CEt·CMe:N·NH·CO·NH_2,

forms a crystalline powder, m. p. 228°, and yields an *acetyl* derivative, $C_8H_{14}O_3N_4$, m. p. 207°.

Pyruvaldehydebis-semicarbazone, $C_5H_{10}O_2N_6$, obtained by the action of an excess of semicarbazide hydrochloride on oximinoacetone, crystallises in slender, lustreless needles, m. p. 254—255° (decomp.). *Acetylpropionylbis-semicarbazone*,

NH_2·CO·NH·N:CMe·CEt:N·NH·CO·NH_2,

obtained from oximinomethyl propyl ketone, has m. p. 250°.

Oximinobenzylideneacetone reacts in the course of several weeks with an aqueous alcoholic solution of semicarbazide, yielding a small amount of a *semicarbazone*,

CHPh:CH·C(:N·NH·CO·NH_2)·CH:N·OH,

m. p. 197° (decomp.).

A bis-semicarbazone could not be obtained. J. J. S.

Electrolysis of Dextrose, Glycerol, and Glycol. Walther Löb [in part with G. Pulvermacher] (*Zeitsch. Elektrochem.*, 1910, **16**, 1—9).—A solution containing from 20 to 60% of dextrose and 5% of sulphuric acid was placed in a porous pot containing a spiral of lead tubing, which was cooled with water and served as anode. The current density was about 0·05 ampere per sq. cm., and the temperature about 16°. The electrolysis was stopped when a comparatively small quantity of the dextrose was oxidised. The changes which occur are interpreted thus: dextrose is first hydrolysed to arabinose and formaldehyde. Dextrose itself is oxidised to gluconic and saccharic acids, arabinose to arabonic and trihydroxyglutaric acids, and formaldehyde to formic acid and carbon monoxide and dioxide. The non-volatile acids were not identified with certainty, as they were separated in the form of a mixture of their calcium salts. When the lead coil is used as cathode instead of anode, the greater part of the dextrose is reduced to mannitol, but formaldehyde and a pentose (yielding an osazone, m. p. 170—172°), were also present in small quantities.

l-Arabinose, when oxidised in the same way as dextrose, yields formaldehyde and a sugar, from which a tetrose has not yet been isolated.

Glycerol yields considerable quantities of formaldehyde and a pentose (probably *i*-arabinose). It is probable that glyceraldehyde is the first product of the oxidation; this is hydrolysed into glycolaldehyde and formaldehyde, and the glycolaldehyde and glyceraldehyde then condense to a pentose. Formic acid is the only volatile acid present, and the non-volatile acids are probably tartronic and trihydroxyglutaric acids, formed by oxidation of glycerol and the pentose respectively. The oxidation of ethylene glycol, under the conditions used for the other substances, yields formaldehyde, formic acid, and carbon dioxide, and minute quantities of a sugar and a non-volatile acid which is not glycollic acid. The sugar was not a pentose, and contained neither dihydroxyacetone, glyceraldehyde, nor glycolaldehyde. It gave an osazone melting at 184—185°, and was probably a hexose. T. E.

The Scission of Sugars. VII. The Reversal of the Sugar Synthesis. WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1909, **23**, 10—26).—The authors have investigated the action of lead hydroxide and sodium hydroxide on sugar solutions under varying conditions. They have isolated formaldehyde, pentose, acetylcarbinol, acetylmethylcarbinol, formic acid, polyhydroxy-acids, and possibly pentitol. Their main conclusions are: the sugar synthesis is a reversible one; formaldehyde and pentose are phases in sugar scission and sugar synthesis; the scission of dextrose into formaldehyde and pentose takes place in solutions, the alkalinity of which corresponds with that of the blood; the reaction also takes place in acid solutions when, owing to oxidation or reduction, the original equilibrium has been disturbed; as shown by the electrolysis of ethylene glycol and glycerol, a sugar synthesis also takes place in acid solutions, from the aldehydes which are then formed by the scission of the sugars. S. B. S.

Kinetic Studies in the Sugar Series. EMIL VOTOČEK and H. NĚMEČEK (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 237—248; *Sitzungsber. böhm. Akad. Wissens.*, 1908).—The rate of action of bromine-water on the aldoses is considerably influenced by their configuration; galactose, for example, is much more rapidly oxidised than dextrose. Lævulose is not acted on by bromine water of low concentration.

The oxidation of aldoses by bromine water is retarded by hydrochloric, hydrobromic, and sulphuric acids.

Dextrose and galactose are both oxidised at the ordinary temperature, being converted quantitatively into gluconic and galactonic acids, and it is probable that the other aldehydic sugars behave in a similar manner.

Aldoses can be distinguished from ketoses by means of the reaction with bromine water. N. H. J. M.

Choraloses. MAURICE HANRIOT (*Ann. Chim. Phys.*, 1909, [viii], **18**, 466—502). A résumé of information, most of which has been published already: chloralose (Abstr., 1893, i, 247; 1894, i, 105); arabinochloralose and xylochloralose (Abstr., 1895, i, 321); galactochloralose and lævulochloralose (Abstr., 1896, i, 519); chloralic acids (Abstr., 1909, i, 206, 287) (compare also Heffter, Abstr., 1889, 845, and Petit and Polonowsky, Abstr., 1894, i, 394). *Mannochloralose*, m. p. 208°, yields an *acetyl* derivative, m. p. 163°, crystallising in large, colourless needles, and a *benzoyl* derivative, m. p. 152°. Mannochloralic lactone, $C_8H_7O_6Cl_3$, is best represented by the formula:

$$O<\begin{array}{l}CH\cdot CH(OH)\cdot O\cdot CH\cdot CCl_3 \\ CH\text{————————}C(OH)\cdot CH<\begin{array}{l}CO\\ O\end{array}\end{array}.$$

For lævulochloralose the following formula is proposed:

$$O<\begin{array}{l}CH\cdot C(OH)(CH_2\cdot OH)\cdot O \\ CH\cdot C(OH)(CH_2\cdot OH)\cdot CH\cdot CCl_3\end{array}.$$

Dibenzoylarabinochloralose has b. p. 275°. Arabinobromalose, prepared like the chloral compound, has m. p. 210°, and occurs in small, indefinite crystals.

The chloralic acids from β-chloralose and xylochloralose are identical, and the crystals are monoclinic [$a:b:c = 1{\cdot}500:1:2{\cdot}628$; $\gamma = 83^\circ$]. Similarly, the chloralic acids from galactochloralose and arabinochloralose are identical (the crystals are rhombic: $a:b:c = 1{\cdot}319:1:0{\cdot}825$). Mannochloralic acid is not isomeric with the other acids of this group. A discussion of isomerism among the chloraloses and their derivatives is given. T. A. H.

The Contraction Occurring when Sucrose is Dissolved in Water. G. FOUQUET (*Bull. Assoc. chim. Sucr. Dist.*, 1909, **27**, 545—549. Compare Abstr., 1908, i, 855).—In reply to statements that contraction does not take place when sucrose is dissolved in water, the author points out that the values determined indirectly for the contraction depend on the density of the sugar dissolved, sucrose having been found to have the two values D 1·5881 and D 1·61. The contraction occurring when a concentrated sugar solution is diluted may be observed by placing about 200 c.c. of the solution in a 500 c.c. flask, and adding water at the same temperature up to the mark, taking care that the two mix as little as possible. On now mixing the water with the sugar solution by rotating the flask, a marked contraction of the total volume will be noticed. The author also shows that in dilute solutions the contraction is approximately proportional to the concentration. W. P. S.

Iron Double Salts of Organic Bases. MAX SCHOLTZ (*Arch. Pharm.*, 1909, **247**, 534—541).—The chlorides of almost all of the metals except iron have been frequently utilised in preparing double chlorides for the characterisation of organic bases. The ferrichlorides are very soluble in water, but are precipitated by concentrated hydrochloric acid as well crystallised compounds of constant composition. The solution of the organic base in the least possible quantity of dilute hydrochloric acid is treated with an excess of ferric chloride, and the mixture is treated slowly with fuming hydrochloric acid until it becomes turbid; after a short time, the crystalline ferrichloride separates. In the case of many aromatic amines, the method is inapplicable, since the hydrochloride of the amine is less soluble than the ferrichloride, and is therefore precipitated first.

The following new ferrichlorides are mentioned (compare Abstr., 1908, i, 202): *diethylamine ferrichloride*, $NHEt_2,HFeCl_4$, m. p. 128°, greenish-yellow prisms; *triethylamine ferrichloride*, $NEt_3,HFeCl_4$, hygroscopic, greenish-yellow needles; *tetraethylammonium ferrichloride*, $(NEt_4)FeCl_4$, groups of light yellow needles, sintering above 240°; *methyltripropylammonium ferrichloride*, $(NMePr_3)FeCl_4$, m. p. 80°, yellow, rhombic crystals; *tributylamine ferrichloride*,

$$N(C_4H_9)_3,HFeCl_4,$$

m. p. 171°, yellow needles; *amylamine ferrichloride*,

$$C_5H_{11}\cdot NH_2,HFeCl_4,$$

yellow needles; *diamylamine ferrichloride*, $NH(C_5H_{11})_2,HFeCl_4$, sinters and melts above 170°, yellow, crystalline powder; *triamylamine ferrichloride*, $N(C_5H_{11})_3,HFeCl_4$, yellow needles; *dibenzylamine ferrichloride*, $NH(C_7H_7)_2,HFeCl_4$, m. p. 145°, yellow prisms; *methylpyridinium*

ferrichloride, $C_5H_5NMe,FeCl_4$, yellow needles; *piperidine ferrichloride*, $C_5NH_{11},HFeCl_4$, m. p. 163°, yellow prisms; *benzylethylconinium ferrichloride*, like the iodide (Abstr., 1904, i, 1044), exists in two forms: the α-form has m. p. 92° and forms yellow needles; the β-form has m. p. 116° and crystallises in compact octahedra; *dibenzylconinium ferrichloride*, $C_8H_{16}N(C_7H_7)_2FeCl_4$, has m. p. 141°; *tetrahydroquinoline ferrichloride*, $C_9NH_{11},HFeCl_4$, m. p. 144°, orange-red, rhombic crystals. The additive compound of tropine and benzyl chloride (Abstr., 1905, i, 79) forms a *ferrichloride*, $C_8H_{15}ON,C_7H_7Cl,FeCl_3$, m. p. 109°, orange-yellow needles. Sparteine hydrochloride forms a *compound*,

$$C_{15}H_{26}N_2,2HCl,FeCl_3,$$

which sinters at 190°, and gradually decomposes. Sparteine methochloride forms the *compound*, $C_{15}H_{26}N_2,MeCl,HCl,FeCl_3$, yellow needles, decomposing above 240°. *o*-Xylylenedipyridinium chloride forms a *compound*, $C_6H_4(CH_2Cl,C_5NH_5,FeCl_3)_2$, m. p. 102°, yellow needles. The additive compound of *o*-xylylene bromide and triethylamine is converted by silver chloride into the chloride, which yields with ferric chloride and hydrochloric acid the *compound*,

$$C_6H_4(CH_2Cl,NEt_3,FeCl_3)_2,$$

m. p. 80°, slender, yellow needles. C. S.

Hexahalogen-irideates. [Iridichlorides and Iridibromides.] ALEXANDER GUTBIER and M. RIESS (*Ber.*, 1909, 42, 4770—4777). —On adding a solution of a substituted ammonium bromide drop by drop to a solution of hydrogen iridichloride in dilute hydrochloric acid at the ordinary temperature, a precipitate of the corresponding substituted ammonium iridichloride is formed. If, however, the solution of hydrogen iridichloride is heated to boiling while the bromide is added, some hydrobromic acid being also present, it changes colour from a reddish-brown, through green, to a deep blue. The formation of the latter colour indicates the change from the iridichloride into the iridibromide. This change can also be brought about by digesting the iridichlorides with dilute hydrobromic acid. The crystals which separate on cooling are not pure, and must be recrystallised from a dilute solution of hydrobromic acid containing free bromine.

The following compounds are described: *Methylammonium iridichloride*, $(NH_3Me)_2IrCl_6$, brownish-red needles. *Dimethylammonium iridichloride*, $(NH_2Me_2)_2IrCl_6$, reddish-brown, rhombic crystals. *Trimethylammonium iridichloride*, $(NHMe_3)_2IrCl_6$, small needles. *Ethylammonium iridichloride*, $(NH_3Et)_2IrCl_6$, brownish-red plates. *Diethylammonium iridichloride*, $(NH_2Et_2)_2IrCl_6$, brownish-red needles. *Triethylammonium iridichloride*, $(NHEt_3)_2IrCl_6$, small needles, which were not obtained pure. n-*Propylammonium iridichloride*,

$$(NH_3Pr^{\alpha})_2IrCl_6,$$

brownish-red needles. iso-*Propylammonium iridichloride*,

$$(NH_3Pr^{\beta})_2IrCl_6,$$

brownish-red needles. n-*Butylammonium iridichloride*,

$$(NH_3C_4H_9)_2IrCl_6,$$

reddish-brown plates. iso-*Butylammonium iridichloride*,

$$(NH_3C_4H_9)_2IrCl_6,$$

brownish-red needles. *Ethylenediammonium iridichloride*, $(C_2H_{10}N_2)IrCl_6$, brownish-red needles. *Propylenediammonium iridichloride*, $(C_3H_{12}N_2)IrCl_6$, reddish-brown crystals. *Pyridinium iridichloride*, $(PyH)_2IrCl_6$, reddish-brown needles. *a-Picolinium iridichloride*, $(C_5NH_5Me)_2IrCl_6$, brownish-red needles. *Quinolinium iridichloride*, $(C_9NH_8)_2IrCl_6$, black, monoclinic prisms, or brownish-red needles. *Benzylammonium iridichloride*, $(C_7H_7 \cdot NH_3)_2IrCl_6$, dark brownish-red plates.

Methylammonium iridibromide, $(NH_3Me)_2IrBr_6$, dark blue octahedra. *Dimethylammonium iridibromide*, $(NH_2Me_2)_2IrBr_6$, dark blue needles. *Trimethylammonium iridibromide*, $(NHMe_3)_2IrBr_6$, dark blue needles. *Ethylammonium iridibromide*, $(NH_3Et)_2IrBr_6$, dark blue plates. *Diethylammonium iridibromide*, $(NH_2Et_2)_2IrBr_6$, dark blue, monoclinic prisms. *Triethylammonium iridibromide*, $(NHEt_3)_2IrBr_6$, dark blue plates. n-*Propylammonium iridibromide*, $(NH_3Pr^{\alpha})_2IrBr_6$, dark blue, six-sided plates. iso*Propylammonium iridibromide*, $(NH_3Pr^{\beta})_2IrBr_6$, dark blue needles. n-*Butylammonium iridibromide*, $(NH_3 \cdot C_4H_9)_2IrBr_6$, dark blue, six-sided plates. iso*Butylammonium iridibromide*, $(NH_3 \cdot C_4H_9)_2IrBr_6$, dark blue plates. *Ethylenediammonium iridibromide*, $(C_2H_{10}N_2)IrBr_6$, deep blue, cubical crystals. *Propylenediammonium iridibromide*, $(C_3H_{12}N_2)IrBr_6$, deep blue prisms. *Pyridinium iridibromide*, $(PyH)_2IrBr_6$, deep blue plates. *a-Picolinium iridibromide*, $(C_5NH_5Me)_2IrBr_6$, dark blue, six-sided, monoclinic plates. *Quinolinium iridibromide*, $(C_9NH_8)_2IrBr_6$, dark blue needles. *Benzylammonium iridibromide*, $(NH_3 \cdot C_7H_7)_2IrBr_6$, dark blue, six-sided plates.

The substituted ammonium iridibromides are not so stable as the alkali iridibromides, and will not withstand prolonged exposure to light. In general, the bromo-salts of the platinum metals are very readily decomposed, both as such, and in solution. T. S. P.

Behaviour of Triethylamine towards Oxidising Agents. T. DAR JUAN (*Amer. Chem. J.*, 1910, **43**, 1—6).—The oxidation of triethylamine may take place either by the direct union of oxygen to form the oxide, $Et_3N:O$, and the subsequent oxidation of this compound to nitric and acetic acids, or by the conversion of the ethylidene groups into acetaldehyde, and the formation of ammonia. In accordance with Nef's view, the latter reaction would take place thus:

$$(C_2H_5)_3N \rightleftharpoons C_2H_4 + NH(C_2H_5)_2 \rightleftharpoons 2C_2H_4 + NH_2 \cdot C_2H_5 \rightleftharpoons 3C_2H_4 + NH_3.$$

Experiments have shown that when triethylamine is oxidised with aqueous solution of potassium permanganate, the carbon residues are converted quantitatively into acetic acid, neither carbonic nor oxalic acid being produced, whilst the nitrogen appears partly as ammonia and partly as nitric acid.

In presence of potassium hydroxide, acetic acid is the chief oxidation product, but oxalic and carbonic acids are also produced. Nitric acid and ammonia are both formed, but the latter is produced in much larger quantity in this case than in the absence of alkali hydroxide. E. G.

Methylated Guanidines. MARTIN SCHENCK (*Arch. Pharm.*, 1909, **247**, 466—490).—Numerous attempts to prepare methylated guanidines by the interaction of guanidine and methyl iodide in methyl alcohol have given unsatisfactory results; the reaction does not proceed to any extent, and usually gives complicated mixtures. However, methylguanidine, $NH:C(NH_2)\cdot NHMe$, and *s*-dimethylguanidine have been isolated as the platinichlorides.

Methyl sulphate and dry guanidine sulphate do not react at the ordinary temperature, or on the water-bath, but at 150—160° the reaction leads to the formation of *s*-dimethylguanidine and a *trimethylguanidine* (*aurichloride*, m. p. 155—156°; *platinichloride*, m. p. 225—226°), which is shown to be the symmetrical compound, $NMe:C(NHMe)_2$, by comparison with a sample obtained by the interaction of *s*-dimethylthiocarbamide, excess of 10% alcoholic methylamine, and mercuric oxide on the water-bath.

The interaction of methyl iodide and the silver derivative of guanidine (prepared by Thiele's method, and also by that of Kutscher and Otori) in methyl alcohol on the water-bath is again unsatisfactory; methylguanidine and *s*-dimethylguanidine have been isolated as the platinichlorides, but the products are mainly mixtures. The author finds that the silver derivative of guanidine, prepared by the methods mentioned, always shows a deficiency of silver.

The methylguanidines obtained by the oxidation of creatine, or of methylglycocyamidine, by the interaction of methylamine and cyanamide, and those isolated from meat extract and urine are all one and the same substance, $NH:C(NH_2)\cdot NHMe$ (*aurichloride*, m. p. 198—200°, yellow needles; *platinichloride*, m. p. 194—195°, orange-red plates). C. S.

Some Guanidine Derivatives. MARTIN SCHENCK (*Arch. Pharm.*, 1909, **247**, 490—506).—Erlenmeyer showed that cyanamide is an intermediate product in the formation of guanidine from cyanogen chloride and alcoholic ammonia. Cyanamide has hitherto not been detected as an intermediate preduct in the reaction between cyanogen iodide and alcoholic ammonia, but by allowing a mixture of the two to remain at the ordinary temperature for several days, the author has detected cyanamide in the reaction product in the form of its characteristic yellow silver derivative. The formation of guanidine, therefore, probably occurs thus: (1) $NCl + 2NH_3 = NC\cdot NH_2 + NH_4I$; (2) $NC\cdot NH_2 + NH_4I = (NH_2)_2C:NH,HI$. By a similar process, cyanogen iodide and 10% alcoholic methylamine (3 mols.), after being heated for several hours in a closed vessel in steam, yield *s*-dimethylguanidine, of which the platinichloride has m. p. 197°, and the aurichloride, 122°. Under the preceding conditions there is practically no reaction between cyanogen iodide and alcoholic dimethylamine. Ethylenedi-

amine ($\frac{1}{2}$—1 mol.), however, yields ethyleneguanidine (2-iminotetrahydroglyoxaline), $\begin{matrix} CH_2\cdot NH \\ | \\ CH_2\cdot NH \end{matrix}\!\!>C\!:\!NH$, of which the *platinichloride*, $2C_3H_7N_3,H_2PtCl_6$, decomposing at 190°, *picrate*, m. p. 219°, and *aurichloride*, $C_3H_7N_3,HAuCl_4$, m. p. 210°, have been prepared. In a similar way, alcoholic propylenediamine (less than 1 mol.) and cyanogen iodide yield propyleneguanidine (2-imino-4-methyltetrahydroglyoxaline), $\begin{matrix} CHMe\cdot NH \\ | \\ CH_2\text{---}NH \end{matrix}\!\!>C\!:\!NH$, the *platinichloride* of which has m. p. 194—195°, and the *aurichloride*, m. p. 100°. Under the some conditions, cyanogen iodide and trimethylenediamine yield a solution from which a crystalline platinichloride, aurichloride, or picrate has not been obtained. Cyanogen iodide and alcoholic aniline, heated in steam for several hours, yield only *p*-iodoaniline (compare Rabe, *Ber.*, 1877, **10**, 1717).

A guanidine derivative has not been obtained by the interaction of cyanogen iodide and glycine or its ethyl ester. C. S.

Glycinamide. MARTIN SCHENCK (*Arch. Pharm.*, 1909, **247**, 506—515).—Glycinamide is best prepared by keeping a mixture of chloroacetamide and ten times the quantity of 30% ammonium hydroxide in a closed vessel for fourteen days; the excess of ammonia is removed by evaporation, by gently warming in a basin, and finally drying the hydrochloride in a desiccator. A solution of the free base is obtained by means of silver oxide. An alcoholic solution of glycinamide is obtained by keeping ethyl glycine and a large excess of 5% alcoholic ammonia in a closed vessel for two to three weeks, then filtering, and freeing the filtrate from the excess of ammonia by a current of dry purified air. A guanidine derivative could not be obtained by the interaction of the aqueous or alcoholic solution of glycinamide and cyanogen iodide either at the ordinary temperature or by heating (compare preceding abstract), owing to the decomposition of the glycinamide into ammonia and glycine. C. S.

New Synthesis of Aminohydroxy-acids and of Piperidone Derivatives. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, **42**, 4878—4892).—The authors show that many ordinary α-bromo-acids, for example, α-bromopropionic, α-bromo*iso*valeric, α-bromo*iso*hexoic, α-bromodihydrocinnamic, are converted to the extent of 70—90% into the hydroxy-acid by boiling their aqueous solutions with calcium carbonate. The reaction has also been applied in the following directions. α-Bromo-δ-*m*-nitrobenzoylaminovaleric acid (Abstr., 1909, i, 303), when boiled with water and calcium carbonate, yields 57% of crystalline *calcium α-hydroxy-δ-*m*-nitrobenzoylaminovalerate*, $Ca(C_{12}H_{12}O_6N_2)_2,4H_2O$, m. p. 80° in its water of crystallisation. The free acid is a yellow oil, which is hydrolysed by boiling barium hydroxide or 5*N*-hydrochloric acid (and subsequent treatment with silver oxide), yielding *δ-amino-α-hydroxyvaleric acid*,

$$NH_2\cdot[CH_2]_3\cdot CH(OH)\cdot CO_2H,$$

m. p. 188—191° (decomp., corr.), which does not form proline by

treatment with hydrochloric acid or a copper salt with copper oxide. It appears to be a general rule that aqueous solutions of α- and β-, but not those of γ-, δ-, or ϵ-, amino-acids yield copper salts by boiling with copper oxide. By esterifying δ-amino-α-hydroxyvaleric acid by methyl alcohol and hydrogen chloride, and dechlorinating the ester-hydrochloride by silver oxide, or better by heating the acid at 190°, the lactam, *3-hydroxy-2-piperidone*, $NH<\begin{matrix}CO\cdot CH(OH)\\CH_2\text{---}CH_2\end{matrix}>CH_2$, m. p. 141—142° (corr.), is obtained, which forms a *platinichloride*, m. p. 160° (decomp.). In a similar manner, by esterification with methyl alcohol and hydrogen chloride and subsequent treatment with silver oxide, δ-aminovaleric acid yields 2-piperidone, and *i*-ornithine yields 3-amino-2-piperidone, which forms a *hydrochloride*, $C_5H_{10}ON_2,HCl$, sintering at 220° and melting completely at 250° (decomp.), *platinichloride*,

$$2C_5H_{10}ON_2,H_2PtCl_6,H_2O,$$

decomposing at 200—205°, *picrate*, m. p. 160—162° (corr.), and is reconverted into ornithine by prolonged heating with 20% hydrochloric acid at 100°.

The following compounds are obtained from α-bromo-ϵ-benzoylaminohexoic acid (Braun, Abstr., 1909, i, 229) by a similar series of reactions: *calcium α-hydroxy-ϵ-benzoylaminohexoate*, a white, crystalline powder; *α-hydroxy-ϵ-benzoylaminohexoic acid*, m. p. 108° (corr.); *ϵ-amino-α-hydroxyhexoic acid*, m. p. 225—230° (decomp., corr.), which does not yield a compound analogous to hydroxypiperidone. C. S.

Catalytic Action of Amino-acids, Peptones, and Proteins in Effecting Certain Syntheses. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, **7**, 49—56).—Many condensations, possibly analogous to those occurring in living cells, may be brought about by the use of amino-acids, peptones, proteoses, or even proteins as catalysts. For example, furfuraldehyde when warmed with malonic acid does not undergo condensation, but if glycine or alanine is added, considerable amounts of furfuracrylic acid are formed. Attempts, however, to bring about certain other types of condensation (for example, the aldol condensation, condensation between aldehydes and ketones, etc.) by the same means failed. W. D. H.

Molybdenum Cyanides. ARTHUR ROSENHEIM, ABRAHAM GARFUNKEL, and F. KOHN (*Zeitsch. anorg. Chem.*, 1909, **65**, 166—177).—Potassium molybdenum cyanide, $K_4Mo(CN)_8,2H_2O$ (Chilesotti, Abstr., 1905, i, 177), contains the only known stable complex ion with a higher co-ordination number than six, and as there is also some doubt as to the valency of the molybdenum, its investigation has been undertaken.

The titration of reduced molybdenum solutions with permanganate is not interfered with by the presence of cyanides if rapidly performed, and the quinquevalence of the molybdenum in these salts is confirmed. A solution containing oxidised molybdenum (Mo^{VI}), manganous salts, and cyanides, however, undergoes a change under the catalytic influence of light, the manganese being partly oxidised by the molybdenum, and the manganous salt of the complex molybdenum

cyanide being precipitated. An excess of permanganate is therefore gradually decolorised if the solutions are exposed to light. The reaction with ammoniacal silver nitrate also proves the molybdenum in $Mo(CN)_8''''$ to be quinquevalent. This can only be brought into harmony with the facts by doubling the molecule, thus making the complex anion $Mo_2(CN)_{16}''''''''$.

A reddish-violet complex salt, $4KCN,MoO_2,10H_2O$, was described by Heide and Hofmann (Abstr., 1896, ii, 605) containing quadrivalent molybdenum. The salts of this series become blue on dehydration. They must contain the complex anion $\left[Mo^{(OH)_4}_{(CN)_4}\right]''''$, in accordance with which they are only formed in strongly alkaline solution. Evaporation with water converts them into blue salts, containing the anion $\left[Mo^{O_2}_{(CN)_4}\right]''''2H_2O$ or $\left[\begin{matrix} O_2 \\ Mo(H_2O)_2 \\ (CN)_4 \end{matrix}\right]$. Alkali cyanides convert the blue salts into the yellow series, $R_8Mo_2(CN)_{16}$, oxidation taking place.

The *manganese* salt of the yellow series, $Mn_2Mo(CN)_8,8H_2O$, forms bright yellow, glistening leaflets. The *silverammine*,

$$[Ag_4(NH_3)_8]Mo(CN)_8,$$

nickelammine, $[Ni(NH_3)_4]_2Mo(CN)_8,8H_2O$, and *pyridinium*,

$$(C_5NH_6)_4Mo(CN)_8,$$

salts are also described. *Hydromolybdicyanic acid*,

$$H_4Mo(CN)_8,6H_2O,$$

is prepared by adding hydrochloric acid, D 1·19, to a concentrated solution of the potassium salt, extracting the precipitate with absolute alcohol, and precipitating with ether in a freezing mixture. The ether oxonium salt is decomposed with water, and precipitated with hydrochloric acid.

The *sodium* salt of the red series, $Na_4[MoO_2(CN)_4]14H_2O$, contains 2 mols. of constitutional water. C. H. D.

Malonyldihydrazones and their Decomposition Products.

CARL BÜLOW and C. BOZENHARDT (*Ber.*, 1909, **42**, 4784—4802).—Analogous to the condensation of malonyldihydrazide with ethyl acetoacetate to ethylmalonylbishydrazoneacetoacetate (Bülow, Abstr., 1908, i, 253), the condensation of a number of substituted esters of 1 : 3-ketocarboxylic acids has been studied.

The ethyl esters of methyl-, ethyl-, *iso*propyl-, and benzylacetoacetates readily condense with malonyldihydrazide to form compounds of the type : $CH_2(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CHR{\cdot}CO_2Et)_2$.

In a similar manner, methyl- and ethyl-malonyldihydrazides react with unsubstituted ethyl acetoacetate to form products :

$$CHR'(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et)_2.$$

On the other hand, it was not found possible to prepare dihydrazones of the type : $CHR'(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CHR{\cdot}CO_2Et)_2$, nor could malonyldihydrazide be coupled with ethyldimethylacetoacetate to form :

$$CH_2(CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CR_2{\cdot}CO_2Et)_2.$$

Apparently alkyl derivatives of this class must contain at least four symmetrically distributed hydrogen atoms.

Ethyl malonylbishydrazoneacetoacetate when boiled with water loses a part of the ethyl acetoacetate, and 3-methyl-5-pyrazolone and an insoluble compound, considered to be a polymeride of *cyclo*malonic acid hydrazide, $CH_2<\begin{matrix}CO\cdot NH\\ | \\ CO\cdot NH\end{matrix}$, are formed. This is difficult to analyse, but forms hydrazine and malonic acid on hydrolysis, and may be synthesised from malonyldihydrazide by prolonged boiling with acetic acid.

Sodium acetate solution acts similarly to water towards ethyl malonylbishydrazoneacetoacetate. Phenylhydrazine decomposes it into malonyldihydrazide and 1-phenyl-3-methyl-5-pyrazolone, which is converted on boiling with ferric chloride into pyrazole-blue. Potassium hydroxide converts it into malonic acid and 3-methyl-5-pyrazolone. Acetic anhydride forms diacetyldimalonylhydrazide; dilute sulphuric acid decomposes it into malonic acid and hydrazine. Benzaldehyde interacts, forming ethyl acetoacetate and bisbenzylidenemalonyldihydrazine.

Resorcinol and cold concentrated sulphuric acid convert it into malonic acid, hydrazine sulphate, and β-methylumbelliferone.

Ethyl malonylbishydrazoneacetoacetate when kept for four months in water at the ordinary temperature decomposes, forming ethyl 3-methyl-5-pyrazolone-4-*iso*propylenecarboxylate, malonic acid, and polymeric *cyclo*malonyl hydrazide. The carboxylic acid when heated is converted into the δ-lactone of 5-hydroxy-3-methylpyrazole-4-*iso*-propylenecarboxylic acid (Abstr., 1908, i, 579), which may also be obtained on slowly heating ethyl malonylbishydrazoacetoacetate in a metallic bath above 125°.

Polymeric cyclo*malonylhydrazide*, $C_3H_4O_2N_2$, is obtained as a grey, amorphous powder, m. p. 266—267°. It is hydrolysed by sodium hydroxide, concentrated sulphuric acid, or sodium acetate to hydrazine and malonic acid.

Ethyl malonylbishydrazonemethylacetoacetate, prepared from malonyldihydrazide and ethyl methylacetoacetate, separates in crystals, m. p. 109—110°.

Ethyl malonylbishydrazone-ethylacetoacetate is a colourless, microcrystalline powder, m. p. 106—106·5°.

*Ethyl malonylbishydrazone*iso*butylacetoacetate* has m. p. 104—105°.

Ethyl malonylbishydrazonebenzylacetoacetate forms colourless needles, m. p. 129—130°.

Ethyl malonylbishydrazoneoxalacetate, prepared from malonyldihydrazide and ethyl oxalacetate, is obtained as a glistening mass of large, matted needles, m. p. 127°.

Ethyl monomethylmalonylbishydrazoneacetoacetate separates in colourless aggregates of snow-like crystals, m. p. 92—93°.

Ethyl monoethylmalonylbishydrazoneacetoacetate, prepared from monoethylmalonyldihydrazide and ethyl acetoacetate, crystallises in small, colourless needles, m. p. 104—104·5°.

Monoethylmalonyldihydrazide is obtained from ethyl monoethylmalonate and hydrazine hydrate in long, matted needles, m. p. 166°.

E. F. A.

Synthesis of Hexahydrocymene [*p*-Methylpropyl*cyclo*hexane]. WLADIMIR A. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1374—1375).—p-*Tolyldimethylcarbinol*, $C_6H_4Me\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on *p*-tolyl methyl ketone, is a colourless liquid with a marked odour, b. p. 109°/15 mm., D_4^{20} 0·9769, n_D^{20} 1·5162. When reduced by means of hydrogen in presence of nickel at 150°, it yields hexahydrocymene [*p*-methylpropyl*cyclo*hexane], $C_{10}H_{20}$, b. p. 170—172°/755 mm., D_4^{20} 0·7974, n_D^{20} 1·4380, which corresponds closely in properties with the menthane obtained by Zelinsky by the reduction of menthene by means of hydrogen in presence of nickel. The investigation is being continued.

T. H. P.

New Space Representation of the Benzene Molecule. JOHN C. EARL (*Chem. News*, 1909, **100**, 305).—The representation in question consists of an octahedron with three sides removed, the remaining sides representing bonds linking the carbon atoms, the linking of the various carbon atoms being the same as in Ladenburg's prism formula. The formula represents satisfactorily the general behaviour of benzene and its derivatives. From it, theoretically only one mono-substitution product, one meta-di- and one para-di-substitution product, but two ortho-disubstitution products, can be formed, and di-, tetra-, and hexa-hydro-derivatives can exist without rupturing the ring.

G. S.

Presence of Ethylene Linkings in Benzene and its Homologues. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1152—1154).—The oxidation of mesitylene by means of air in presence of powdered sodium hydroxide (compare Abstr., 1909, i, 154, 471) yields 1·17% of a monobasic acid, $C_9H_{11}\cdot CO_2H$, formed by the oxidation of one of the methyl groups. With *o*-, *m*-, and *p*-xylenes, under similar conditions, only very small proportions of acids are obtained. Hence, the degree of oxidisability of benzenoid hydrocarbons is independent of isomerism in the aromatic nucleus. This result, which is partly confirmed by the investigations on cymene and ψ-cymene, supports the conclusion that ethylene linkings are absent from benzene and its homologues, quite independently of the position of the substituent groups. These observations appear to give final confirmation to the diagonal structural formula for benzene and its homologues, which is supported by thermochemical data and by the action of reducing agents, such as hydrogen iodide, the reduction being accompanied by complete transformation of the six-membered ring into one containing five members. The author regards the supposed support given to the Kekulé formula by the action of ozone on benzene and its homologues as ill-founded, the compounds formed as the result of such action being peroxidic in character.

T. H. P.

Derivatives of Phenyldi*cyclo*hexylmethane. MARCEL GODCHOT (*Compt. rend.*, 1909, **149**, 1137—1139).—When phenyldi*cyclo*hexylmethane (Abstr., 1909, i, 19) is dissolved in fuming nitric acid, it undergoes conversion into *nitrophenyldi*cyclo*hexylmethane*,

$$NO_2\cdot C_6H_4\cdot CH(C_6H_{11})_2,$$

pale yellow needles, m. p. about 113°.

Phenyldicyclohexylcarbinol, $CPh(C_6H_{11})_2 \cdot OH$, has been obtained by the action of ethyl benzoate on magnesium *cyclo*hexyl bromide; it crystallises in prisms, m. p. 77°, and also with 1½ mols. alcohol in prisms, m. p. 55°. Unlike triphenylcarbinol, it does not combine with aniline, phenol, or hydroxylamine. When distilled in a vacuum, the carbinol loses water, yielding a *hydrocarbon*, $C_6H_{11} \cdot CPh:C_6H_{10}$. *Dinitrophenyldicyclohexylmethane*, $NO_2 \cdot C_6H_4 \cdot C(C_6H_{11})_2 \cdot NO_2$, m. p. 150°, arises from the action of fuming nitric acid on the foregoing carbinol, whilst under the same conditions the hydrocarbon yields a *mononitro*-derivative, m. p. 130°. W. O. W.

Carbonium Perchlorates. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, **42**, 4856—4865).—Coloured salts and molecular compounds of triphenylcarbinol and its derivatives have recently received much attention in connexion with the problem of colour and constitution, but hitherto salts of triphenylcarbinol and oxy-acids have not been obtained in a crystalline form directly from their components. The authors find that perchloric acid yields beautifully crystalline derivatives with triphenylcarbinol, phenolphthalein, fluorescein, and distyryl ketone. The acid is a 71% solution, obtained by evaporating the commercial acid until the temperature is 136° and then distilling.

Hydrated *triphenylmethyl perchlorate*, $CPh_3 \cdot ClO_4, H_2O$, is obtained by adding 6 c.c. of 71·5% perchloric acid to an ethereal solution of 2 grams of the carbinol. It crystallises in deep yellow octahedra with a blue shimmer, and decomposes by heating or by the addition of water. *Triphenylmethyl perchlorate*, $CPh_3 \cdot ClO_4$, obtained by the addition of 71% perchloric acid to a cold solution of the carbinol in acetic-anhydride, crystallises in octahedra, which are brownish-yellow to brownish-red by transmitted light and blue by reflected light. The same substance is apparently produced when a mixture of perchloric acid and ethereal triphenylmethyl chloride is evaporated over sulphuric acid; when the evaporation is performed in an atmosphere of hydrogen chloride, citron-yellow octahedra with a blue lustre are obtained of a mixed salt, $2CPh_3 \cdot Cl, CPh_3 \cdot ClO_4$.

Phenolphthalein perchlorate, $C_{20}H_{14}O_4 \cdot ClO_4, H_2O$, obtained from its components, forms dichroic crystals, which are ruby-red by transmitted and pale blue by reflected light; it is instantly decomposed by water. *Fluorescein diperchlorate*, $C_{20}H_{12}O_5, 2HClO_4$, obtained in a similar manner, is a yellow powder.

[With H. LECHER.]—*Distyryl ketone perchlorate*, $C_{17}H_{14}O, HClO_4$, is precipitated as a red powder by the addition of 71% perchloric acid to ethereal distyryl ketone. After being dried in a vacuum over phosphoric oxide, the substance is orange-red; it is instantly decomposed by water. C. S.

Cryoscopy of Organic Mixtures and Additive Compounds. ABEL BUGUET (*Compt. rend.*, 1909, **149**, 857—858).—Additive compounds of acenaphthene with α-trinitrotoluene and 2 : 4-dinitrotoluene melt at 109° and 60° respectively, and the compound of phenanthrene with α-trinitrotoluene at 84°. Complete freezing-point curves of

mixtures of these hydrocarbons and nitro-compounds take the form of a W, showing two eutectics and a maximum at the compound.

In the following cases, no compound being formed, the freezing-point curve is a V, showing one eutectic: phenanthrene with 2 : 4-dinitrotoluene and α-nitronaphthalene; acenaphthene with *p*-nitrotoluene; naphthalene with *p*-nitrotoluene, α-nitronaphthalene, acenaphthene, benzoic acid, salicylic acid, azobenzene, diphenylamine, guaiacol, chloral hydrate, menthol, methyl oxalate, phenanthrene, salol, and thymol.

R. J. C.

p-Hydroxyphenylethylamine. KARL W. ROSENMUND (*Ber.*, 1909, **42**, 4778—4783. Compare Barger, Trans., 1909, **95**, 1123, 2193).—A relatively simple synthesis of *p*-hydroxyphenylethylamine is effected by condensing anisaldehyde with nitromethane to β-nitro-*p*-methoxystyrene, which can be directly reduced to *p*-methoxyphenylethylamine. It is preferable first to isolate the oxime of *p*-methoxyphenylacetaldehyde and reduce this to the amine. The methoxyl group is eliminated by boiling with decolorised hydriodic acid. The base is obtained by this method in good yield and in a pure state.

β-*Nitro*-p-*methoxystyrene*, $OMe\cdot C_6H_4\cdot CH\!:\!CH\cdot NO_2$, crystallises in long, yellow needles, m. p. 86—87°. It may be reduced with aluminium amalgam, or with zinc dust and acetic acid, to the oxime of *p*-methoxyphenylacetaldehyde, m. p. 120°, which is conveniently further reduced with sodium amalgam and alcoholic acetic acid. p-*Methoxyphenylethylamine* has a fish-like odour, b. p. 136—138°/18 mm. It forms a *carbonate* on exposure to the atmosphere. The hydrochloride has m. p. 207°.

p-Hydroxyphenylethylamine was obtained in glistening, colourless needles or plates, m. p. 160°; the *hydroiodide* forms yellow needles.

E. F. A.

Molecular Weights of Liquid Diphenylamine, Triphenylamine, and Aniline Hydrochloride. MARIE PRZYLUSKA (*J. Chim. Phys.*, 1909, **7**, 511—533. Compare Renard and Guye, Abstr., 1907, ii, 334).—The surface-tensions of the three substances have been measured by Ramsay and Shield's method at a number of temperatures between their melting and boiling points. Diphenylamine distilled at atmospheric pressure gave irregular results, but after fractional distillation at 50 mm. pressure, the surface-tensions indicated a unimolecular constitution. The somewhat different conclusion arrived at by Dutoit and Friderich (Abstr., 1900, ii, 194) may have been due to products of decomposition in their material.

Diphenylamine gives normal b. p. elevations in benzene or acetone, whereas Kahlenberg found it to be dissociated in acetonitrile. The surface-tension of diphenylamine indicates that its critical temperature would be 560° if it were not decomposed by heat.

Triphenylamine is polymerised to an increasing degree as the temperature rises from 108° to 335°, in agreement with the known tendency of such hydrocarbons to give condensation products on heating. Aniline hydrochloride passes directly at its boiling point (243°) from a polymerised liquid to a dissociated gaseous form.

R. J. C.

Action of Thiocarbimides on Alcohols and Mercaptans. I. New Method for Obtaining Mono-substituted Thio- and Dithiocarbamates of Monatomic Alcohols and Mercaptans. M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1438—1454. Compare Abstr., 1909, i, 300).—Methyl phenylthiocarbamate, prepared by the action of sodium methoxide on phenylthiocarbimide, has m. p. 92·5—93·5° (Orndorff and Richmond, Abstr., 1900, i, 156, gave 97°). The corresponding ethyl derivative has m. p. 68—69° (Orndorff and Richmond, *loc. cit.*, gave 71—72°).

Allyl phenylthiocarbamate, $NHPh\cdot CS\cdot O\cdot C_3H_5$, forms aggregates of long needles, m. p. 64·5—65·5°; the *menthyl* ester,

$$NHPh\cdot CS\cdot O\cdot C_{10}H_{19},$$

has m. p. 74—75°, $[\alpha]_D^{20}$ −63·07°; the *benzyl* ester,

$$NHPh\cdot CS\cdot O\cdot CH_2Ph,$$

has m. p. 82—82·5°.

Methyl β-naphthylthiocarbamate, $C_{10}H_7\cdot NH\cdot CS\cdot OMe$, prepared by the action of sodium methoxide on β-naphthylthiocarbimide, forms pale, cinnamon-coloured crystals, m. p. 104—105°. The *propyl* ester has m. p. 83—84°.

Methyl allylthiocarbamate, $C_3H_5\cdot NH\cdot CS\cdot OMe$, obtained by the action of sodium methoxide on allylthiocarbimide, is a brownish-yellow, mobile liquid with a peculiar odour, b. p. 121—122°/27 mm., D_{20}^{20} 1·0811, D_4^{20} 1·0792, n_D^{20} 1·5379; it combines readily with bromine, giving a crystalline product.

Bornyl allylthiocarbamate, $C_3H_5\cdot NH\cdot CS\cdot O\cdot C_{10}H_{17}$, forms white crystals, m. p. 59—60°, $[\alpha]_D^{20}$ +14·25°.

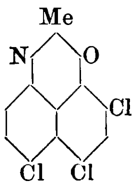
Methyl phenyldithiocarbamate, $NHPh\cdot CS\cdot SMe$, prepared by the interaction of methyl mercaptan and phenylthiocarbimide in presence of sodium hydroxide, has m. p. 95—96° (compare Will, Abstr., 1882, 723; Losanitsch, Abstr., 1892, 55). The *ethyl* ester has m. p. 60—61° (Hofmann, *Ber.*, 1869, **2**, 120, gave 56°, and Will, Abstr., 1882, 1088, gave 60°). The *propyl* ester,

$$NHPh\cdot CS\cdot SPr^a,$$

which may be prepared either in aqueous solution or in absence of water, has m. p. 66—67°.

Methyl β-naphthyldithiocarbamate, $C_{10}H_7\cdot NH\cdot CS\cdot SMe$, has m. p. 116—117°. T. H. P.

8-Amino-1-naphthol. II. FRITZ FICHTER and THEODOR KÜHNEL (*Ber.*, 1909, **42**, 4748—4752. Compare Abstr., 1906, i, 839).—Chlorine reacts with an acetone solution of 8-acetylamino-1-naphthol in much the same manner as bromine (*loc. cit.*, 840), yielding a crystalline precipitate of 6 : 7 : 9-*trichloro*-2-*methylperinaphthoxazole* (annexed formula) in the form of greenish-coloured needles, which do not melt below 300°.



8-Acetylamino-1-naphthoxyacetic acid,

$$NHAc\cdot C_{10}H_6\cdot O\cdot CH_2\cdot CO_2H,$$

obtained by condensing 8-acetylamino-1-naphthol with a concentrated aqueous solution of chloroacetic acid and potassium hydroxide, forms long, colourless needles, m. p. 245°. The *cupric* salt, $(C_{14}H_{12}O_4N)_2Cu$,

forms slender, pale blue needles. When boiled with alkalis or acids, the acid does not yield a ring compound as the isomeric 1-acetylamino-2-naphthoxyacetic acid does (Spitzer, Abstr., 1901, i, 715).

The nitro-derivative obtained by the action of nitric acid on 8-acetylamino-1-naphthyl acetate is now shown to be the 5-nitro-derivative. This has been proved by hydrolysing the product to nitro-8-acetylamino-1-naphthol, the methyl ether of which when hydrolysed, diazotised, and boiled with alcohol gives the same methyl ether as is obtained by the action of methyl sulphate on 5-nitro-1-naphthol (Kaufler and Bräuer, Abstr., 1907, i, 799). 5-Nitro-8-acetylamino-1-naphthol changes colour at 192°, but has m. p. 240°

4-*Benzeneazo*-5-*nitro*-8-*acetylamino*-1-*naphthol*, $C_{18}H_{14}O_4N_4$, obtained by condensing benzenediazonium chloride with an alcoholic alkaline solution of the 5-nitro-8-acetylamino-1-naphthol, forms dark red crystals with a metallic lustre and m. p. 220°.

5-*Nitro*-8-*amino*-1-*naphthyl methyl ether*, $C_{11}H_{10}O_3N_2$, forms large, reddish-brown crystals, m. p. 193°. 5-*Nitro*-1-*naphthyl methyl ether*, $C_{11}H_9O_3N$, forms slender, yellow needles, m. p. 96—97°.

When α-naphthyl acetate is nitrated at 0° with nitric acid (D 1·38), a 60% yield of 2:4-dinitro-1-naphthol and a 5% yield of 2-nitro-1-naphthyl acetate are obtained.

8-*Tolylsulphonylamino*-1-*naphthol*, $OH{\cdot}C_{10}H_6{\cdot}NH{\cdot}SO_2{\cdot}C_7H_7$, obtained by heating 8-amino-1-naphthol sulphate, *p*-toluenesulphonyl chloride, and sodium acetate with acetic acid, forms colourless prisms, m. p. 189°.

8-*Acetylamino*-1-*naphthyl ethyl ether*, $OEt{\cdot}C_{10}H_6{\cdot}NHAc$, crystallises in broad, glistening plates, m. p. 154. J. J. S.

Compounds of Hexamethylenetetramine with Multivalent Alcohols. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1324—1325).—Hexamethylenetetramine reacts with multivalent alcohols, forming crystalline, complex compounds, which are deposited in almost quantitative yield when aqueous solutions of the amine and alcohol are mixed.

Resorcinol gives the *compound*, $C_6H_{12}N_4,C_6H_4(OH)_2$, which forms shining, oblique prisms, begins to turn yellow at 125°, and decomposes completely at about 200°.

Catechol yields the *compound*, $C_6H_{12}N_4,2C_6H_4(OH)_2$, in slender needles, decomp. about 160°.

Pyrogallol gives the *compound*, $2C_6H_{12}N_4,3C_6H_3(OH)_3$, forming small needles, decomp. about 145°. T. H. P.

Tertiary Alcohols of the Tolylallyl Series. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1326—1332. Compare Abstr., 1909, i, 151).—p-*Tolylethylallylcarbinol*,

$$C_6H_4Me{\cdot}CEt(CH_2{\cdot}CH{:}CH_2){\cdot}OH,$$

prepared by the action of magnesium on a mixture of *p*-tolyl ethyl ketone and allyl bromide, is a yellow, viscous liquid with an intense, characteristic odour, b. p. 133—135°/18 mm., D_4^{22} 0·9664, n_D^{22} 1·52093. On oxidation, it gives the corresponding acid and trihydric alcohol, to be described later.

The intermediate *organo-magnesium compound*,

$C_6H_4Me{\cdot}CEt(C_3H_5){\cdot}O{\cdot}MgBr,OEt_2$,

formed in the above reaction, separates in almost colourless prisms.

p-*Tolylpropylallylcarbinol*, $C_6H_4Me{\cdot}CPr^{\alpha}(C_3H_5){\cdot}OH$, prepared by the action of magnesium on a mixture of *p*-tolyl propyl ketone and allyl bromide, is a viscous, colourless liquid with an intense, characteristic odour, b. p. 138—139°/13 mm., D_4^{20} 0·9531, n_D^{20} 1·51682.

p-*Tolylisopropylallylcarbinol*, $C_6H_4Me{\cdot}CPr^{\beta}(C_3H_5){\cdot}OH$, obtained by the action of magnesium on a mixture of *p*-tolyl *iso*propyl ketone and allyl bromide, is a viscous, colourless liquid of aromatic odour, b. p. 140—143°/21 mm., $D_4^{19\cdot5}$ 0·9542, $n_D^{19\cdot5}$ 1·51385.

Comparison of the physical constants of these alcohols and those of *p*-tolylmethylallylcarbinol (*loc. cit.*) shows that passage from any one member of the series to the next higher homologue is accompanied by a rise of 5—7° in the b. p., a diminution of 0·017—0·013 in the value of D, an increase in the value of *n*, and an increase of about 5 in the molecular refraction (Lorenz and Lorentz's formula). Isomeric alcohols of this series differ but slightly in b. p., and have almost identical values for D and for the molecular refraction.

T. H. P.

Action of Magnesium on a Mixture of Allyl Bromide and Benzophenone: Synthesis of Diphenylallylcarbinol. B. TARASOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1309—1313).—Diphenylallylcarbinol, $C_3H_5{\cdot}CPh_2{\cdot}OH$ (compare Javorsky, Abstr., 1908, i, 753), is a viscous, pale yellow liquid with a characteristic odour and a bitter taste, b. p. 300°/760 mm. (decomp.), 183—184°/27 mm., $D_4^{23\cdot8}$ 1·0720, $n_D^{23\cdot8}$ 1·59179. It decolorises bromine readily, and on oxidation with 1·5 times the theoretical proportion of potassium permanganate, yields *αα-diphenylbutane-αγδ-triol*,

$OH{\cdot}CPh_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$,

which crystallises in small, pale yellow, hygroscopic needles, m. p. 136—137°.

More vigorous oxidation of diphenylallylcarbinol (1 mol.) by means of permanganate (4 atoms of oxygen) yields β-hydroxy-ββ-diphenylpropionic acid (compare Rupe and Busolt, Abstr., 1908, i, 23).

In one instance the action of magnesium on a mixture of allyl bromide and benzophenone yielded, instead of diphenylallylcarbinol, a product which, when distilled under diminished pressure, gave water and then a heavy, dark red liquid, b. p. about 290—292°, with a characteristic hydrocarbon odour. T. H. P.

Action of Magnesium on a Mixture of Phenyl *p*-Tolyl Ketone and Allyl Bromide. W. KUZMIN (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1314—1319).—*Phenyl*-p-*tolylallylcarbinol*,

$C_6H_4Me{\cdot}CPh(OH){\cdot}CH_2{\cdot}CH{:}CH_2$,

obtained by the action of magnesium on a mixture of allyl bromide and phenyl *p*-tolyl ketone, is a colourless liquid, b. p. 201—202°/30 mm.

*α-Phenyl-α-*p*-tolylbutane-αγδ-triol*,

$$C_6H_4Me\cdot CPh(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

prepared by oxidising phenyl-*p*-tolylallylcarbinol with 1% permanganate solution, forms nodular crystals, m. p. 149—150°.

*β-Hydroxy-β-phenyl-β-*p*-tolylpropionic acid*,

$$C_6H_4Me\cdot CPh(OH)\cdot CH_2\cdot CO_2H,$$

prepared by oxidising phenyl-*p*-tolylallylcarbinol by means of 4% permanganate solution, forms rosettes or nodular masses of acicular crystals, and begins to decompose at 181°. Its *silver*, *potassium*, and *copper* salts were prepared. T. H. P.

Structure of Naphthenic Acids. K. W. Charitschkoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1150—1152).—The structure of the naphthenic acids isolated from natural naphtha still remains undecided, descriptions which have been given of these acids often containing no information concerning either their characteristic reactions or their derivatives. These acids exhibit distinctly acid properties, forming stable salts with many metallic oxides, and, in some cases, displacing mineral acids, for example, from copper and silver salts; whilst, on the other hand, they present the properties of anhydrides and alcohols, as they give Rosenthaler's reaction with hydrochloric acid and vanillin, and form chloro-anhydrides, which are decomposed with difficulty by water, or an alkali yielding the corresponding acids, together with compounds of unknown constitution resembling simple ethers. The formula,

$$\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>CH\cdot[CH_2]_4\cdot CH<\!\!\begin{array}{l} CH_2 \\ O \end{array}\!\!>CH\cdot OH,$$

given by Zalozetzky, and the one,

$$\begin{array}{l} CH_2\cdot CHMe \\ |\qquad\qquad | \\ CH_2—CH_2 \end{array}\!\!>CH\cdot CH<\!\!\begin{array}{l} CH_2\cdot CH_2 \\ \qquad\quad | \\ O——CH\cdot OH \end{array},$$

given by Brun (Wischin, *Die Naphtene*, 28), and also other formulæ which have been given for decanapthenic acid, do not explain the acidic function possessed by the hydroxyl group.

The suggestion is made that *cyclo*hexane-3-acetic acid,

$$C_6H_{11}\cdot CH_2\cdot CO_2H$$

(compare Zelinsky and Alexandroff, Abstr., 1902, i, 74), may be capable of existing in a tautomeric modification having the formula

$$C_6H_{11}\cdot CO\cdot CH_2\cdot OH,$$

which would explain the alcoholic properties exhibited by the acid. T. H. P.

Synthesis of Aromatic Amino-acids. IV. Direct Carboxylation of Dimethylaniline in the Nucleus. Rearrangement of Alkylphenylcarbonates into *p*- and *o*-Alkylaminobenzoates. Josef Houben and Robert Freund (*Ber.*, 1909, **42**, 4815—4825).—The formation of dimethylaminobenzoic acid when methylaniline, alkyl iodide, magnesium and carbon dioxide are heated at 200° in presence of dimethylaniline suggests that the last substance acts as a methylating agent, and that possibly the introduction of the group CO_2MgI into the nucleus of methylaniline facilitates the

methylation of the methylamino-group. On the other hand, no methylaminobenzoate is formed on prolonged heating of magnesium aminobenzoate with dimethylaniline. Probably magnesium methyl-iodide and dimethylaniline first interact, forming methane and iodo-magnesiumdimethylaniline, $IMg \cdot C_6H_4 \cdot NMe_2$, and this forms an additive compound with carbon dioxide, yielding the *p*-dimethylamino-benzoate. In agreement with this hypothesis, the salt of *p*-dimethyl-aminobenzoic acid is formed when *p*-toluidine, dimethylaniline, and methyl magnesium iodide are heated in a stream of carbon dioxide at 190—200°. *p*-Dimethylaminobenzoic acid is formed when magnesium methyl iodide and dimethylaniline are heated in carbon dioxide at 215° in open vessels or under pressure. The formation of an inflammable gas, probably methane, was also observed.

No salt of *p*-dimethylaminobenzoic acid is formed when dimethyl-aniline is heated with iodomagnesium acetate or formate, with or without carbon dioxide; this disposes of the possibility that carbon dioxide and magnesium methyl iodide first react to form iodo-magnesium acetate.

p-Dimethylaminobenzoic acid is the main product when carbon dioxide and methylaniline magnesium iodide are heated under considerable pressure, but at the same time small quantities of an *o*-methylamino-acid are formed, crystallising in well formed blue, glistening needles, and fluorescing blue in alcoholic solution; this is probably methylanthranilic acid.

On heating carbon dioxide and ethylaniline magnesium iodide, a mixture of *p*-diethylaminobenzoic acid, m. p. 193°, and *p*-ethyl-aminobenzoic acid, together with traces of methylanthranilic acid, is obtained.

When carbon dioxide is heated at 220° under 10 atmospheres pressure with magnesium ethyl iodide and a mixture of mono- and di-ethylaniline, both *p*-diethylaminobenzoic acid, m. p. 190°, and p-*ethylaminobenzoic acid*, m. p. 177—178°, are formed. p-*Acetyl-ethylaminobenzoic acid* forms colourless platelets, m. p. 180°; the *chloroacetyl* derivative also crystallises in colourless, flat plates, m. p. 163—164°; the *carbethoxy*-compound separates in needles, m. p. 130°. E. F. A.

Benzylamineacrylic Acids (ω-Aminomethylcinnamic Acids). ALFRED EINHORN and MAXIMILIAN GÖTTLER (*Ber.*, 1909, 42, 4837—4850).—Methylolchloroacetamide and cinnamic acid interact in presence of concentrated sulphuric acid, forming a mixture of ω-chloroacetylamino-*p*- and -*m*-methylcinnamic acids. The two iso-merides may be separated by means of acetone, in which the para-derivative is sparingly soluble.

Ethyl ω-chloroacetylamino-*p*-methylcinnamate interacts with diethyl-amine or piperidine, forming ethyl ω-diethyl- or piperidyl-glycylamino-*p*-methylcinnamate, which is hydrolysed by hydrobromic acid to the corresponding acid.

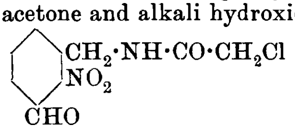
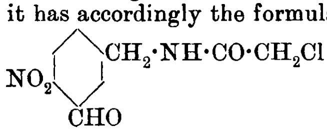
When boiled with hydrochloric acid, ω-chloroacetylamino-*p*-methyl-cinnamic acid is converted into the hydrochloride of ω-amino-*p*-methyl-cinnamic acid, from which the free acid is obtained on evaporation

with ammonia. ω-Amino-*p*-methylcinnamic acid forms terephthalic acid on oxidation with permanganate; nitrous acid converts it into *p*-methylolcinnamic acid.

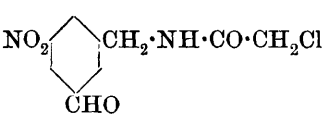
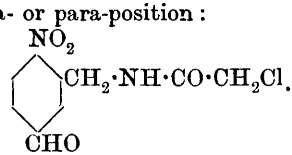
On nitration of ω-chloroacetylamino-*p*-methylcinnamic acid, a mixture of two isomeric mononitro-acids, m. p. 171—172° and 224—225°, is formed.

The less fusible acid is converted into a nitro-ω-chloroacetylamino-*p*-tolualdehyde on oxidation, which, since it is coloured blue by acetone and alkali hydroxide, contains the nitro- and COH-groups in the adjacent positions; therefore it must be *o*-nitro-ω-chloroacetylamino-*p*-methylcinnamic acid; the more fusible isomeride is *m*-nitro-ω-chloro-acetylamino-*p*-methylcinnamic acid.

Two mononitro-derivatives are similarly formed from ω-chloroacetyl-amino-*m*-methylcinnamic acid, m. p. 220° and 198° respectively. The latter gives on oxidation nitro-ω-chloroacetylamino-*m*-tolualdehyde, which forms a claret-red phenylhydrazone and gives a blue coloration with acetone and alkali hydroxide; it has accordingly the formula:


or


The nitro-acid, m. p. 220°, is the main product; it forms a nitro-aldehyde giving a greenish-red colour with acetone and alkali, and has accordingly the nitro-group in the meta- or para-position:


or


Cinnamic acid is dissolved in much concentrated sulphuric acid, and methylolchloroacetamide slowly added in the cold; about 70% of the theoretical quantity of the condensation product is obtained. Permanganate oxidises it into a mixture of terephthalic and *iso*phthalic acids, identified by their dimethyl esters. By treatment with acetone the product is separated into *ω-chloroacetylamino-*p*-methylcinnamic acid*, $CO_2H\cdot CH{:}CH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, crystallising in well formed needles, m. p. 210°, and *ω-chloroacetylamino-*m*-methylcinnamic acid*, which separates in starch-like, crystalline aggregates, m. p. 152—155°. The *ethyl* ester of the former crystallises in bunches of intergrown needles, m. p. 106—107°; the *methyl* ester has m. p. 96—97°.

*Ethyl ω-diethylglycylamino-*p*-methylcinnamate*,

$$CO_2Et\cdot CH{:}CH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2,$$

was obtained as an oil on condensation of the above ester with diethylamine; the *salts* were also oily, with the exception of the *picrate*, which crystallises in golden-yellow plates, m. p. 152°. The *hydrobromide* of the corresponding acid crystallises in fatty, glistening plates, m. p. 211—212°.

*Ethyl ω-piperidylglycylamino-*p*-methylcinnamate* is a thick fluid oil; the *picrate* crystallises from alcohol in platelets, m. p. 170°. The *hydrobromide* of the acid crystallises in glistening plates, m. p. 226—227°.

*ω-Amino-*p*-methylcinnamic acid*, $NH_2\cdot CH_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$,

crystallises in plates, which do not melt at 320°. The *hydrochloride* forms stellar aggregates of lustrous needles, m. p. 295—296°. The acid interacts with monochloroacetic anhydride, forming the ω-chloroacetyl described above.

ω-Amino-m-*methylcinnamic acid* crystallises in prismatic needles, which darken at 200°, m. p. 243—244° (decomp.). The *hydrochloride* forms quadratic plates or rhomboids.

p-*Methylolcinnamic acid*, $OH\cdot CH_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, prepared by the action of sodium nitrite on the amino-*p*-methylcinnamic acid separates in indefinite, flocculent aggregates or needles, m. p. 200—201°.

2-*Nitro-ω-chloroacetylamino*-p-*methylcinnamic acid* crystallises in colourless needles, m. p. 224—225°; the *ethyl* ester forms very minute needles, m. p. 143—144°.

3-*Nitro-ω-chloroacetylamino*-p-*tolualdehyde* crystallises in minute rhombohedra, m. p. 171° (decomp.). When warmed with concentrated hydrochloric acid, it becomes at first violet-red, later a dirty green, and subsequently a black powder separates. The *phenylhydrazone* forms garnet-red prisms, m. p. 191—192° (decomp.). The aldehyde condenses with acetone in presence of sodium hydroxide to *diketopiperazinobis* (o-*nitro*-p-*methylstyryl methyl ketone*),

$$C_4N_2H_4O_2[CH_2\cdot C_6H_3(NO_2)\cdot CH{:}CH\cdot COMe]_2,$$

crystallising in matted needles, which darken at 230°, m. p. 242° (decomp.).

3-*Nitro-ω-chloroacetylamino*-p-*methylcinnamic acid* forms strongly refractive plates, m. p. 171—172°; the *ethyl* ester forms rectangular platelets, m. p. 105°.

4- or 5′-*Nitro-ω-chloroacetylamino*-m-*methylcinnamic acid* crystallises in needles, m. p. 220°; the *ethyl* ester separates in prisms, m. p. 148—150°.

5- or 6-*Nitro-ω-chloroacetylamino*-m-*tolualdehyde* forms refractive parallelogram-like plates, m. p. 198—199°, and gives an intense red coloration with acetone and alkali. o-*Nitro-ω-chloroacetylamino*-m-*methylcinnamic acid* crystallises in leaflets, m. p. 198°; the *ethyl* ester forms refractive platelets, m. p. 241—242° (decomp.). o-*Nitro-ω-chloroacetylamino*-m-*tolualdehyde* forms bunches of needles, m. p. 125°; it gives an intense blue coloration on warming with acetone and sodium hydroxide. The *phenylhydrazone* crystallises in needles aggregated in bunches, m. p. 174°. E. F. A.

Some Condensation Products from Arylsulphonated Acetonitriles and Aromatic Aldehydes. JULIUS TRÖGER and H. BREMER (*Arch. Pharm.*, 1909, **247**, 613—617).—The following compounds have been obtained by the method described previously (Abstr., 1908, i, 798); the notation is the same, namely,

$$R\cdot CH{:}C(SO_2R')\cdot CN.$$

$R = p\text{-}C_6H_4\cdot NMe_2$, $R' = Ph$, red needles with blue fluorescence, 194°; $R = p\text{-}C_6H_4Pr^{\beta}$, $R' = Ph$, pale yellow needles, 78°; $R = p\text{-}C_6H_4\cdot OH$, $R' = Ph$, yellowish-white crystals, 214°; $R = p\text{-}C_6H_4\cdot NMe_2$, $R' = \beta\text{-}C_{10}H_7$, red crystals, 197°; $R = p\text{-}C_6H_4Pr^{\beta}$, $R' = \beta\text{-}C_{10}H_7$, large prisms,

146°; R = p-$C_6H_4 \cdot OH$, R′ = β-$C_{10}H_7$, yellow crystals, 157°; R = p-$C_6H_4 \cdot NH_2$, R′ = p-C_6H_4Cl, red rhombohedra, 245—246°;

R = p-$C_6H_4 \cdot OH$, R′ = p-C_6H_4Cl,

yellow prisms, 154—156°; R = p-$C_6H_4 \cdot NMe_2$, R′ = p-C_7H_7, red crystals with blue fluorescence, 217°; R = p-$C_6H_4 \cdot OH$, R′ = p-C_7H_7, leaflets, 133—135°; R = p-$C_6H_4NMe_2$, R′ = p-C_6H_4Br, red prisms with blue shimmer, 240—241°; R = p-$C_6H_4 \cdot OH$, R′ = p-C_6H_4Br, yellow prisms, 166°; R = p-$C_6H_4 \cdot NMe_2$, R′ = p-C_6H_4I, ruby-red crystals with blue shimmer, 222°; R = p-$C_6H_4 \cdot NMe_2$, R′ = $C_6H_2Me_3$, light red prisms, 192°; R = p-$C_6H_4 \cdot OH$, R′ = $C_6H_2Me_3$, yellow prisms, 181°.

C. S.

Halogen-amino-acids. VIII. Position of the Iodine Atoms in Di-iodotyrosine (Iodogorgonic Acid). HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1910, **43**, 11—19).—Wheeler and Jamieson (Abstr., 1905, i, 350) synthesised iodogorgonic acid, and showed it to be a di-iodotyrosine, probably the 3 : 5-compound. This configuration has now been confirmed.

Di-iodotyrosine, when treated with methyl iodide and potassium hydroxide, is converted into a *compound*, provisionally regarded as $OMe \cdot C_6H_2I_2 \cdot CH_2 \cdot CH(NMe_3I) \cdot CO_2H$. On boiling this substance with sodium hydroxide, *sodium* 3 : 5-*di-iodo*-p-*methoxycinnamate* is obtained, and, when acidified with hydrochloric acid, is converted into the corresponding *acid*, $OMe \cdot C_6H_2I_2 \cdot CH{:}CH \cdot CO_2H$, m. p. 202—203°, which forms minute prisms or long, silky needles. This acid has also been prepared by the methylation of 3 : 5-di-iodo-p-hydroxycinnamic acid (Paal and Mohr, Abstr., 1897, i, 53), which has m. p. 247° (decomp.). The *potassium*, *barium*, *silver*, *mercury*, and *copper* salts of 3 : 5-di-iodo-p-methoxycinnamic acid are described. The *methyl* ester, m. p. 173—174°, crystallises in thin plates, and the *ethyl* ester, m. p. 135°, in small, colourless prisms. E. G.

Conversion of Stable Stereoisomeric Ethylene Derivatives into the Labile Modifications by Ultraviolet Light. RICHARD STOERMER (*Ber.*, 1909, **42**, 4865—4871).—In connexion with the stereoisomerides of substituted ethylenes, the conversion of the labile into the stable modification by the action of light, particularly in the presence of a halogen, is not uncommon. The converse change, produced by light alone, has been remarked in very few cases (Paal and Schultze, Abstr., 1902, i, 228; Ciamician and Silber, *ibid.*, 1904, i, 161).

Perkin has noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight (Trans., 1881, **39**, 409), but the author finds that in the coumaric acid series the tendency is the other way, the stable form changing to the labile under the influence of ultraviolet light. Thus Perkin's change occurs only to the extent of 25%, whereas coumaric acid yields 75% of coumarin, methylcoumaric acid yields 75% of methylcoumarinic acid, ethylcoumaric acid yields ethylcoumarinic acid quantitatively, and acetylcoumaric acid is also quantitatively changed to acetylcoumarinic acid.

That the changes are caused by the ultraviolet rays is proved by

means of light filters, the interposition of a filter which absorbs ultraviolet light between the lamp and the solution preventing any change of the stable to the labile modification. Hence the less fusible stable forms of stereoisomeric compounds can be changed directly, under definite conditions, into the more reactive labile modifications if energy is supplied by ultraviolet light. Thus the stable form of *o*-anisylcinnamic acid, which could not be changed into the labile modification by Stoermer and Frederici (Abstr., 1908, i, 179), has now been converted to the extent of 50% by using a more intense light. In the case of stereoisomeric α-alkylated acids, the conversion of the stable into the labile form is a matter of great difficulty. The case of cinnamic acid is interesting. A benzene solution of ordinary cinnamic acid is exposed for eight days to the light of a Uviol lamp, with the result that 25—30% of Liebermann's *iso*cinnamic acid, m. p. 58°, is produced. *allo*Cinnamic acid in benzene is converted into ordinary cinnamic acid under similar conditions. Also fumaric acid changes to maleic acid in eight days, but the conversion of mesaconic acid into citraconic acid is very difficult, these being α-methylated acids. When stilbene in benzene is exposed to ultraviolet light for eight days, it is converted to the extent of about 90% into *iso*stilbene, which can be reconverted into stilbene by heating at 170—180° for one hour, by the vapour of fuming nitric acid in a few minutes, and quantitatively by exposure to sunlight of its solution in carbon disulphide containing a trace of bromine.

C. S.

General Synthesis of Phenylated Fatty Acids. FERDINAND MAUTHNER (*Annalen*, 1909, **370**, 368—375. Compare Abstr., 1908, i, 986).—Derivatives of acetic acid, containing as a substituent either a phenyl or substituted phenyl group, may be prepared from the corresponding aromatic aldehydes by the following series of changes: (1) $R\cdot CHO + NHBz\cdot CH_2\cdot CO_2H = 2H_2O + NBz<\begin{matrix}CO\\ |\\ C{:}CHR\end{matrix}$; (2) $NBz<\begin{matrix}CO\\ |\\ C{:}CHR\end{matrix} \xrightarrow[NaOH]{Aqueous} NH_3 + Ph\cdot CO_2H + CH_2R\cdot CO\cdot CO_2H$, and (3) $CH_2R\cdot CO\cdot CO_2H + H_2O_2 = H_2O + CO_2 + CH_2R\cdot CO_2H$. The isolation of the substituted pyruvic acid is unnecessary; the solution obtained by boiling the azlactone with a dilute aqueous solution of sodium hydroxide is treated with hydrogen peroxide at the ordinary temperature. In order to exemplify its general applicability, phenylacetic acid, *p*-hydroxyphenylacetic acid, *o*-methoxyphenylacetic acid, *p*-methoxyphenylacetic acid, homovanillic [4-hydroxy-3-methoxyphenylacetic] acid, and homopiperonic [methylenedioxyphenylacetic] acid have been prepared by this method.

The following azlactones are prepared by heating the necessary aldehyde with hippuric acid, acetic anhydride, and sodium acetate on a water-bath. 3-*Acetoxy*-4-*methoxy*-(α)-*benzoyliminocinnamic anhydride*, $C_{19}H_{15}O_5N$, has m. p. 194—195°. 2-*Methoxy*-(α)-*benzoyliminocinnamic anhydride*, $C_{17}H_{13}O_3N$, crystallises in yellow leaflets, m. p. 165—166°.

W. H. G.

Lactonoid Anhydrides of Acylated Amines. I. The Lactones of Acetylanthranoylanthranilic Acid and of Acetylanthranilic Acid. ERNST MOHR and FRIEDRICH KÖHLER (*J. pr. Chem.*, 1909, [ii], 80, 521—546).—Anthranoylanthranilic acid, when boiled with excess of acetic anhydride, yields the lactone,

$$NHAc\cdot C_6H_4\cdot C{<}{\scriptstyle N\cdot C_6H_4 \atop \scriptstyle O\cdot CO}\text{,}$$

and not acetylanthranoylanthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57). The formation of this characteristic lactone is one of the best criteria for the recognition of anthranoylanthranilic acid.

Anthranilic acid or acetylanthranilic acid, when heated with acetic anhydride, yields acetylanthranil, ${CMe{:}N \atop O{-}CO}{>}C_6H_4$ (Bredt and Hof, Abstr., 1900, i, 229; Anschütz and Schmidt, *ibid.*, 1903, i, 56), and benzoylanthranilic acid yields a similar lactone (Angeli and Angelico, Abstr., 1901, i, 46; Heller and Fiesselmann, *ibid.*, 1902, i, 780). Thionyl chloride transforms anthranoylanthranilic acid into a lactone, m. p. 162° (Schroeter, Abstr., 1907, i, 530), which reacts with acetic anhydride, yielding acetylanthranoylanthranilic acid lactone.

Benzoylated α-amino-fatty acids are also capable of losing water in a similar manner, yielding lactones (Erlenmeyer, Abstr., 1893, i, 580; 1899, i, 759; 1900, i, 549; compare also Mohr and Geis, Abstr., 1908, i, 339, and Mohr and Stroschein, *ibid.*, 1909, i, 581).

These lactones are intermediate in properties between acid anhydrides and lactones, and belong to Hans Meyer's second class of lactones (Abstr., 1900, i, 9). They combine readily with ammonia, yielding amides of the type $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, which lose the elements of water when boiled with sodium hydroxide solution, yielding cyclic imides, for example, $NHAc\cdot C_6H_4\cdot C{<}{N{-}C_6H_4 \atop NH\cdot CO}$.

The possibility of a lactam structure, $NHAc\cdot C_6H_4\cdot CO\cdot N{<}{C_6H_4 \atop CO}$, for the lactone of acetylanthranoylanthranilic acid is discussed, but rejected (compare Bamberger, Abstr., 1903, i, 432; 1909, i, 509).

Acetylanthranoylanthranilic acid crystallises in colourless needles, m. p. 221·5—222° (Anschütz, Schmidt, and Greiffenberg, 225—226°). The *sodium* salt crystallises in thin, flexible needles. The *lactone*, $NHAc\cdot C_6H_4\cdot C{<}{N\cdot C_6H_4 \atop O\cdot CO}$, crystallises in pale yellow plates or needles, m. p. 211—212°. When warmed with sodium hydroxide solution, it yields ultimately acetic and anthranilic acids. When boiled with alcoholic ammonia, the lactone yields *acetylanthranoylanthranilamide*, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, which crystallises in glistening, snow-white prisms, m. p. 226—227° (decomp.). The *imide*, 2-*o*-*aminophenyl*-3 : 4-*dihydro*-1 : 3-*quinazolone*, $NH_2\cdot C_6H_4\cdot C{<}{N{-}C_6H_4 \atop NH\cdot CO}$, obtained by boiling the above amide with $6N$-sodium hydroxide solution and precipitating with acetic acid, crystallises in lemon-

yellow needles, m. p. 237°, and has both feebly basic and acidic properties. The *sodium* salt and the *hydrochloride* have been prepared.

The *acetyl* derivative, $C_{16}H_{13}O_2N_3$, crystallises in very pale yellow prisms, m. p. 278° (decomp.), and yields a sparingly soluble *sodium* derivative.

The name lactimones (Abstr., 1908, i, 339 ; 1909, i, 581) for this type of lactone is withdrawn. J. J. S.

Lactonoid Anhydrides of Acylated Amino-acids. II. Lactone of α-Benzoylamino*iso*butyric Acid. ERNST MOHR [with THEODOR GEIS] (*J. pr. Chem.*, 1910, [ii], 81, 49—73. Compare Abstr., 1908, i, 339).—A more detailed account of work already published. The lactimone, $CMe_2<\begin{smallmatrix}N=CPh\\ CO\cdot O\end{smallmatrix}$ (*loc. cit.*), is a very reactive substance, yielding *α-benzoylaminoisobutyranilide*,

$NHBz\cdot CMe_2\cdot CO\cdot NHPh$,

m. p. 228—229°, with aniline; the *chloride*, $NHBz\cdot CMe_2\cdot COCl$, m. p. 148—150° (decomp.), with dry hydrogen chloride, and *α-benzoylamino-isobutyrylglycine*, $NHBz\cdot CMe_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 191°, by heating with glycine at 140—170°.

Ethyl α-benzoylaminoisobutyrate has m. p. 123°, and the *methyl* ester, m. p. 124°. C. S.

Condensation of *p*-Hydroxybenzoic Acid with Formaldehyde. FELIX EPSTEIN (*J. pr. Chem.*, 1910, [ii], 81, 85—93).—The interaction of *p*-hydroxybenzoic acid, 40% formaldehyde, and dilute hydrochloric acid for eight to ten hours on the water-bath results in the formation of 2 : 2'-*dihydroxydiphenylmethane*-5 : 5-*dicarboxylic acid*, $[CO_2H\cdot C_6H_3(OH)]_2CH_2$, an ill-defined substance which carbonises by heating and does not yield crystalline derivatives; the *copper* salt, $C_{15}H_{10}O_6Cu,3H_2O$, and the *diacetyl* derivative, $C_{19}H_{16}O_8$, have been prepared. By prolonged heating with concentrated sulphuric acid, it is converted into a green *sulphoxanthinedicarboxylic acid*, $C_{15}H_{10}O_8S$, which forms a green *copper* salt, $(C_{15}H_7O_8S)_2Cu_3$. C. S.

New Method of Preparing Ellagic Acid. L. V. BUSCHUEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1484—1488).—The action of Berthollet's salt and hydrochloric acid on protocatechuic acid yields katellagic acid, whilst gallic acid under the same treatment gives ellagic acid. T. H. P.

Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide. CONRAD WILLGERODT and WILHELM HAMBRECHT (*J. pr. Chem.*, 1910, [ii], 81, 74—85).—The behaviour of *p*-tolyl alkyl ketones is exactly analogous to that of phenyl alkyl ketones in the reaction described previously (Abstr., 1909, i, 716) provided the conditions therein mentioned are strictly adhered to. The yields of amide and acid are less the greater the carbon content of the alkyl groups, and the preparation of fatty

aromatic acids by means of Willgerodt's reaction reaches its limit between the valeryl and the heptyl ketones.

p-Tolyl methyl ketone and yellow ammonium sulphide at 220° give 45% of *p*-tolylacetamide and 8—10% of *p*-tolylacetic acid, whilst with colourless ammonium sulphide, 2 : 5-di-*p*-tolylthiophen and 2 : 4-di-*p*-tolylthiophen are obtained in addition to the preceding amide and acid. Similarly, *p*-tolyl ethyl ketone and yellow ammonium sulphide at 210° yield 30% of *p*-tolylpropionamide and 6—8% of the corresponding acid. p-*Tolyl propyl ketone*, $C_7H_7{\cdot}COPr^{\alpha}$, b. p. 247—248°, prepared from butyryl chloride and toluene in carbon disulphide in the presence of aluminium chloride, forms a *phenylhydrazone*, m. p. 73°, and by the Willgerodt reaction at 210° yields 18—20% of p-*tolylbutyramide*, m. p. 135°, and 5% of p-*tolylbutyric acid*, m. p. 60°, of which the *barium* and *silver* salts are described. *p*-Tolyl *iso*propyl ketone and yellow ammonium sulphide at 200° yield p-*tolyl*iso*butyramide*, m. p. 130°, and a very small amount of p-*tolyl*iso*butyric acid*, m. p. 85°. p-*Tolyl* iso*butyl ketone*, $C_7H_7{\cdot}CO{\cdot}CH_2{\cdot}CHMe_2$, b. p. 254—255°, obtained from toluene and *iso*valeryl chloride, forms an *oxime*, m. p. 65°, and yields 3—4% of p-*tolyl*iso*valeramide*, m. p. 150°, and a very slight trace of the *acid*, m. p. 128°, in the Willgerodt reaction at 190°. p-*Tolyl butyl ketone*, m. p. 17°, b. p. 261°, and yellow ammonium sulphide at 180° yield 2% of p-*tolylvaleramide*, m. p. 113°, and an unappreciable quantity of the corresponding acid. C. S.

Preparation of Benzophenoneimine Derivatives. G. REDDELIEN (*Ber.*, 1909, **42**, 4759—4762).—A good yield of benzophenonephenylimine (diphenylmethyleneaniline; Pauly, this Journ., 1877, ii, 614; Graebe, Abstr., 1899, i, 702; Nägeli, *ibid.*, i, 910) can be prepared by condensing aniline and benzophenone with anhydrous zinc chloride at 160—180° for half an hour. Substituted anilines can react in a similar manner, and the stability of the product increases with the presence of negative substituents.

Diphenylmethylene-p-*toluidine*, $CPh_2{:}N{\cdot}C_6H_4Me$, is a viscid oil, and has b. p. 228°/15 mm., 245°/30 mm., or 360°/atm. pres.

The isomeric *meta*-derivative crystallises in rectangular, pointed prisms, m. p. 82·5°.

Diphenylmethylene-3 : 4-*xylidine*, $CPh_2{:}N{\cdot}C_6H_3Me_2$, forms rhombic plates, m. p. 122°.

Diphenylmethylene-m-*nitroaniline*, $CPh_2{:}N{\cdot}C_6H_4{\cdot}NO_2$, crystallises in yellow cubes or hexagonal plates, m. p. 123·5°. *Diphenylmethylene*-p-*aminophenol*, $CPh_2{:}N{\cdot}C_6H_4{\cdot}OH,C_2H_5{\cdot}OH$, forms yellow plates, m. p. 172°, and loses its alcohol of crystallisation at 110°. It is stable towards hydrolysing agents.

Diphenylmethylenedimethyl-p-*phenylenediamine*, $CPh_2{:}N{\cdot}C_6H_4{\cdot}NMe_2$, forms compact, orange-yellow crystals, and melts at 85° to a turbid, brown liquid, which clarifies at 93°.

A by-product, obtained in the preparation of the aniline derivative, is the zinc compound, $2NH_2Ph,ZnCl_2,2H_2O$ (Lachowicz and Bandrowski, Abstr., 1888, 1281). J. J. S.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. V. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. I. FRITZ STRAUS [and, in part, A. ACKERMANN and GEORG LUTZ] (*Annalen*, 1909, 370, 315—367. Compare Straus and Ecker, Abstr., 1906, i, 859; Straus and Caspari, Abstr., 1907, i, 609; Straus and Ackermann, Abstr., 1909, i, 489; Straus and Hüssy, Abstr., 1909, i, 490).—The present communication deals mainly with the difference in the reactivity of the halogens in distyrylchlorobromomethane and *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane. These substances, prepared by the action of acetyl bromide or hydrogen bromide and calcium bromide on the corresponding chloro-carbinols dissolved in benzene, are distinctly yellow, a further example of the analogy between these ketohalides and triphenylmethyl halides.

The chlorobromides are strictly analogous with the corresponding keto-chlorides in their chemical properties; for example, the power of one of the ethylene linkings to add on halogen is completely lost; the benzylideneacetophenone derivative does not combine with bromine, and distyrylchlorobromomethane combines only with 1 mol. of bromine; further, the group $>CClBr$ reacts in all cases so that only one atomic proportion of the halogen takes part in the change; thus, one mol. of the chlorobromide when acted on by water or methyl alcohol yields one mol. of hydrogen halide, about 96% of which is hydrogen bromide, the remainder being hydrogen chloride; similarly, an equivalent of halogen is eliminated from *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane when treated with an excess of silver oxide; the product is a mixture of the corresponding chlorocarbinol (about 98%) and bromocarbinol.

The rate at which the halogen in triphenylbromomethane, distyrylchlorobromomethane, diphenyldibromomethane, *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane, and the corresponding chloro-compounds is replaced by hydroxyl (compare Straus and Hüssy, *loc. cit.*) has been investigated; it is found that the reaction velocity decreases in the order given, and that the bromo-compounds are decomposed far more rapidly than the corresponding chloro-compounds.

The chlorobromides dissolve in concentrated sulphuric acid with the elimination of hydrogen halide; the reddish-violet solutions probably contain complex salts of the two sulphates, $RR_1CCl\cdot SO_4H$ and $RR_1CBr\cdot SO_4H$, with sulphuric acid; in support of this assumption it is found that the absorption spectra of the solutions differ slightly from those of the corresponding keto-chlorides. The solutions of the chlorobromides in liquid sulphur dioxide are more intensely coloured than those of the keto-chlorides, indicating a greater degree of ionisation, which probably takes place in two directions, $RR_1CCl \mid Br$ and $RR_1CBr \mid Cl$, but mainly in the manner indicated by the first formula.

Triphenylchloromethane when acted on by a *N*/4-solution of hydrogen bromide in benzene is converted into the corresponding bromo-compound to the extent of about 85%; the reaction is a reversible one, a state of equilibrium being reached in about five minutes. Similarly, the chlorine is largely replaced by bromine when

a solution of the chloro-compound in benzene is shaken with calcium bromide; this reaction is likewise reversible. The interaction of keto-chlorides with hydrogen bromide and with calcium bromide is of a more complex character; a solution of distyryldichloromethane in benzene containing hydrogen bromide is found to contain part of this substance in equilibrium with the corresponding chloro-bromide and di-bromide, as represented by the equation: $(CHPh\dot{:}CH)_2CCl_2 + 2HBr \rightleftarrows (CHPh\dot{:}CH)_2CClBr + HBr + HCl \rightleftarrows (CHPh\dot{:}CH)_2CBr_2 + 2HCl$. Calcium bromide is found to react in a similar manner. On the other hand, when a solution of distyrylchlorobromomethane in benzene is treated with a slight excess of silver chloride, it is converted completely into the corresponding keto-chloride; this is in complete accord with the behaviour of triphenylbromomethane towards silver chloride.

The investigation has been extended to a study of the behaviour of tertiary butyl chloride and the corresponding bromide towards water, hydrogen halides, and calcium halides. It is found that these compounds are decomposed rapidly by water, and undergo reversible double decomposition when treated with a dissimilar hydrogen halide; the bromide interacts to a small extent with calcium chloride, but the chloride is not attacked by calcium bromide.

The different reactivity of the halogen atoms in the keto-chlorides and chloro-bromides is regarded by the author as due to a different form of union between the carbon atom and the two halogen atoms, the replaceable halogen being joined to the carbon by an ionogenetic valency ("*ionogene Valenz*"); accordingly, the bromo-chlorides and keto-chlorides are to be regarded as solid solutions of two valency isomerides in a state of equilibrium; this may be represented in the case of distyrylchlorobromomethane thus: $(CHPh\dot{:}CH)_2CCl\sim\sim\sim Br \rightleftarrows (CHPh\dot{:}CH)_2CBr\sim\sim\sim Cl$.

The bearing of the results obtained in this investigation on the question of the constitution of the triphenylhalogenmethanes is discussed, and the views of Baeyer (Abstr., 1909, i, 641) and Gomberg (Abstr., 1907, i, 504; 1909, i, 144) adversely criticised.

p-*Chlorophenyl*-p-*chlorostyrylchlorobromomethane*, $C_{15}H_{10}Cl_3Br$, crystallises in compact, pale yellow prisms, m. p. 98·5—99·5°; dilute solutions in liquid sulphur dioxide are violet-red, more concentrated solutions are pale yellow; a solution of the substance with stannic chloride in nitrobenzene is bluish-red.

Distyrylchlorobromomethane, $C_{17}H_{14}ClBr$, crystallises in stellate groups of large, slender, glistening, yellow leaflets, m. p. 91—92°; the *dibromide*, $C_{17}H_{14}ClBr_3$, crystallises in radially-grouped, colourless prisms and decomposes at 165—166°; the *mercuribromide*, $C_{17}H_{14}ClBr,4HgBr_2$, is a crystalline, green powder. W. H. G.

The Pyrogenetic Decomposition of (1) β-Benzopinacolin and (2) α-Benzopinacolin. Maurice Delacre (*Bull. Soc. chim.*, 1909, [iv], 5, 1144—1149, 1149—1153).—Both products were first carefully purified and then heated in retorts, the products of distillation being collected and separated by fractional distillation, and finally by crystallisation from appropriate solvents, where necessary. Full details of these separations are given in the original papers.

β-Benzopinacolin yielded triphenylmethane, *p*-benzoyltriphenylmethane, tetraphenylethylene, "needles," benzene, benzaldehyde, benzophenone, and unidentified products boiling at 240—320°, 340—430°, and 405—440°, and some carbonaceous residue.

α-Benzopinacolin furnished substantially the same products, with the addition of "yellow needles" and unidentified products of somewhat different boiling points. The relative yields of the various substances were not the same in the two cases. An unidentified substance, showing violet fluorescence, was present in both sets of distillation products. The "needles" were isolated from the fractions boiling at 325—380° and 380—405; this material had m. p. 144°, and may be identical with Hemilian's hydrocarbon, $C_{19}H_{14}$. The "yellow needles" obtained from α-benzopinacolin came from the same fractions as the "needles"; this product had m. p. 245°, and contained carbon, 78·8%, and hydrogen, 4·5%. T. A. H.

Action of Acetic Anhydride on Octabromo-1′-hydroxy-1-methoxy-*o*-quino-1-monoxide. C. LORING JACKSON and H. A. FLINT (*Amer. Chem. J.*, 1910, **43**, 7—11).—Jackson and Porter (Abstr., 1904, i, 254) and Jackson and Carlton (Abstr., 1905, i, 907) have shown that tetrabromo-*o*-quinone readily unites with methyl alcohol to form a compound, termed the methyl α-compound, which, when boiled with methyl alcohol, is converted into an isomeric or β-compound. Jackson and MacLaurin (Abstr., 1907, i, 223) have found that the α-compound is octabromo-1′-hydroxy-1-methoxy-*o*-quino-1-monoxide, and that the β-compound is octabromo-1′-hydroxy-1-methoxy-*o*-quino-1 : 2 : 2-trioxide. These authors also found that by the action of acetic anhydride on the α-compound, two substances were produced, one of which was yellow and had m. p. 225°, whilst the other was white and had m. p. 218°.

A further study of the yellow compound has shown that, when pure, it has m. p. 244° (decomp.), and that it is identical with heptabromo-*o*-quinocatechol hemi-ether (Jackson and Russe, Abstr., 1906, i, 288). On treating this substance with hot acetic anhydride, it is converted into hexabromo-*o*-quinocatechol ether (Jackson and Koch, Abstr., 1901, i, 597). When heptabromo-*o*-quinocatechol hemi-ether is shaken with 10% solution of sodium hydroxide, a *substance*, m. p. about 240° (decomp.), is obtained, which forms white, rhombic crystals. E. G.

Aminoanilide and Certain New Dianilides of α-Naphthaquinone. OSWALD MILLER and J. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1420—1421).—In acetic acid solution, amino-imino-α-naphthaquinone (di-iminonaphthol) hydrochloride is converted by aromatic amines into the corresponding dianilides:

$$C_6H_4<\begin{matrix}CO\text{——}C\cdot NH_2\\ \quad\quad\quad\;\; \| \\ C(NH)\cdot CH\end{matrix} + 2NH_2Ph = 2NH_3 + C_6H_4<\begin{matrix}CO\text{——}C\cdot NHPh\\ \quad\quad\quad\;\; \| \\ C(NPh)\cdot CH\end{matrix}$$

The reaction probably takes place in two stages, the first of these resulting in the formation of an aminoanilide of α-naphthaquinone, $C_6H_4<\begin{matrix}CO\text{——}C\cdot NH_2\\ \| \\ C(NR)\cdot CH\end{matrix}$. The authors find that these intermediate aminoanilides, which have not been described previously, are obtained

when the reaction between the aromatic amine and the di-imino-naphthol hydrochloride takes place in alcoholic solution, in which the velocity of formation of dianilide from aminoanilide is less than that of the aminoanilide itself.

The aminoanilides of α-naphthaquinone are coloured, crystalline compounds, readily soluble in alcohol or dilute acid; in most cases they exhibit softening before melting. The following compounds of this type have been obtained in the pure state.

Aminoanilide, brown prisms or red needles, m. p. 121°. *Amino-*o-*toluidide*, red needles, m. p. 115°. *Amino-*m-*toluidide*, red needles, m. p. 110°. *Amino-*p-*toluidide*, red needles, m. p. 122·5°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 2 : 4), red prisms or needles, m. p. 144°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 3 : 4), pale red prisms or needles, m. p. 160°. *Amino-xylidide* (Me : Me : NH_2 = 1 : 4 : 5), reddish-brown needles, m. p. 153°. *Amino-ψ-cumidide*, red needles, m. p. 155°.

The following new dianilides of α naphthaquinone have also been prepared. *Di-*o-*toluidide*, orange prisms or needles, m. p. 123·5°. *Di-*m-*toluidide*, red needles, m. p. 147°. *Dixylidide* (1 : 2 : 4), reddish-brown prisms or needles, m. p. 184°. *Dixylidide* (1 : 3 : 4), reddish-brown prisms, m. p. 154° (?). *Dixylidide* (1 : 4 : 5), reddish-brown prisms or needles, m. p. 114° (?). T. H. P.

Action of Piperidine on *d*-Pinene Chloro-oxime. L. V. Buschueff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1481—1484).—The action of piperidine on the chloro-oxime of *d*-pinene isolated from Russian turpentine yields (1) nitrosopinene, agreeing in all its properties with that obtained by Golubeff (Abstr., 1908, i, 902) from the *l*-pinene of the ethereal oil of the Siberian fir; (2) pinene nitrol-piperidine (compare Wallach, Abstr., 1888, 1098). T. H. P.

Conversion of Pulegone into Menthenes. Karl Auwers (*Ber.*, 1909, **42**, 4895—4907).—3-Chloro*iso*terpinolene (from pulegone), when reduced with sodium and amyl alcohol, yields, not the expected *iso*-terpinolene, but a mixture of Δ^{3}- and $\Delta^{4(8)}$-menthene. Hence this reduction forms an exception to the general rule regarding the addition of hydrogen to conjugated double linkings. R. V. S.

Matico Leaves and Matico Oils. Hermann Thoms (*Arch. Pharm.*, 1909, **247**, 591—612).—Commercial matico oils rarely have the same or a similar composition, because they are prepared from various kinds of *Piper*, the constituents of which vary considerably. The author has prepared and examined matico oils from botanically individual leaf-material. Japan camphor and borneol, hitherto undetected in matico oils, have been discovered in the oil from *Piper camphoriferum*. On the contrary, cineol, parsley apiole, asarone, and matico camphor, which have frequently been found in commercial oils, could not be detected by the author in his oils. Dillapiole is present in particularly large amount in the oil from the leaves of *Piper acutifolium* var. *subverbascifolium*. C. S.

The Essential Oil of Hyacinths. C. J. Enklaar (*Chem. Weekblad*, 1910, **7**, 1—11).—When distilled at 10 mm. pressure, the

essential oil of hyacinths yields three fractions, distilling respectively below 90°, at 92—94°, and between 94° and 150°. The first fraction contains a very volatile substance of disagreeable odour. When evaporated over concentrated sulphuric acid, it develops a red colour. The second fraction contains an unknown *substance* of powerful odour, its formula being probably $C_{15}H_{20}O$. It has b. p. 205—206°/760 mm., D^{15} 0·907, n_D^{16} 1·4914, and forms 50% of the oil. The third fraction contains benzyl benzoate and other esters (20% of the oil), an unknown fluorescent substance which is free from nitrogen (5%), and benzyl alcohol with other primary alcohols (1%). A. J. W.

Decomposition of Amygdalin. KARL FEIST (*Arch. Pharm.*, 1909, **247**, 542—545. Compare Abstr., 1909, i, 589).—The synthetic production of *d*-benzaldehydecyanohydrin by the action of emulsin on benzaldehyde and hydrogen cyanide is a more rapid process, according to Auld (Trans., 1909, **95**, 927), than its formation by the decomposition of amygdalin by emulsin, thus indicating that its formation in the latter reaction is due to a secondary and not to a primary reaction. Since these results are exactly the reverse of those obtained previously by the author, he has repeated his experiments without adding dextrose, and confirms Auld's results. The emulsin used was obtained from Kahlbaum, that in the former experiments from Schuchardt. Since Rosenthaler (Abstr., 1908, i, 817) has shown that emulsin contains a hydrolysing and also a synthesising enzyme, the discrepancy between the author's two series of experiments is attributed to the fact that Kahlbaum's emulsin contains a preponderance of the synthesising enzyme, and Schuchardt's of the hydrolysing enzyme.

The author still maintains, however, that *d*-benzaldehydecyanohydrin is a primary product of the decomposition of amygdalin by emulsin, because emulsin, freed from the synthesising enzyme by Rosenthaler's method (Abstr., 1909, i, 622), acting on amygdalin and also on a mixture of benzaldehyde and hydrogen cyanide, produces in the former case a slightly dextrorotatory solution, whilst in the latter the solution remains inactive. Moreover, Walker and Krieble have shown that the decomposition of amygdalin by sulphuric acid yields dextrose and benzaldehydecyanohydrin (Trans., 1909, **95**, 1369), and the author finds that when amygdalin is treated with 2·77*N*-sulphuric acid for three hours at 98° and extracted with benzene, the solution, although dark coloured, is distinctly dextrorotatory. C. S.

Crystalline Chitosan Sulphate. EMIL LÖWY (*Biochem. Zeitsch.*, 1909, **23**, 47—60).—The chitosan was prepared from the shells of *Nephrops norvegicus*, from the chitin of which the chitosan was obtained by heating at 170—180° with potassium hydroxide. The hydrochloride, hydrobromide, and sulphate were prepared by allowing hot solutions of the chitosan in the respective acids to cool. The concentration of the acids must be fairly high, as the chitosan is readily soluble in dilute acids. The salts were obtained crystalline. The analyses of the sulphate correspond with the formula

$$C_{28}H_{50}O_{19}N_4(H_2SO_4)_3.$$

It can form additive products with bromine and iodine, taking up the

halogen in the proportion of one chlorine or bromine atom to two of nitrogen. It yields on hydrolysis (the products of which were quantitatively estimated) glucosamine and acetic acid, and it is assumed that the chitosan is a polymeric form of monoacetyldiglucosamine, and that the hydrolysis can be represented by the equation: $(C_{28}H_{50}O_{19}N_4)_x + 5xH_2O = 4x(C_6H_{13}O_5N) + 2x(CH_3{\cdot}CO_2H)$.

S. B. S.

Formation of Phlobaphens. MAXIMILIAN NIERENSTEIN and T. A. WEBSTER (*Collegium*, 1909, 337—341).—Mangrove tannin is oxidised by oxygen, hydrogen peroxide, or potassium persulphate solution, yielding phlobaphens. The phlobaphen formed when oxygen is used, gave anthracene when distilled with zinc dust (compare Abstr., 1908, i, 40). The hydrogen peroxide oxidation product gave diphenylmethane when distilled with zinc, and the phlobaphen obtained by oxidising the tannin with an acetic acid solution of potassium persulphate in the presence of sulphuric acid, gave anthracene when distilled with zinc dust. The latter compound is termed *β-phlobaphen*, and the product which yields diphenylmethane, *α-phlobaphen*. The α-compound when boiled with dilute sulphuric acid yields the β-derivative. It is probable that this conversion is accompanied by the elimination of water and the formation of an anthraquinone skeleton.

J. J. S.

Constituents of the Rhizome of Imperatoria. JOHANNES HERZOG and D. KROHN (*Arch. Pharm.*, 1909, **247**, 553—591).—The paper deals with a comparative examination of the crystalline constituents of the rhizomes of *Imperatoria* and *Peucedanum*. Earlier workers have shown that the latter contains peucedanin and oxypeucedanin (Schmidt, Abstr., 1899, i, 377), whilst the former contains ostruthin, oxypeucedanin, but not peucedanin (Gorup-Besanez, Abstr., 1874, 907; 1877, 717; Jassoy, Abstr., 1890, 1154). Oxypeucedanin has only once been found in the rhizome of *Imperatoria* (Heut, Abstr., 1875, 772), and then in such small amount that its identity with the oxypeucedanin of *Peucedanum* has not been certainly established.

Using their former method (Abstr., 1908, ii, 978), the authors extract the rhizomes of *Imperatoria* with boiling benzene, concentrate the extract, and treat it with light petroleum, whereby a viscous mass is separated which soon becomes crystalline. The mass is treated with ether, and the oxypeucedanin thus obtained is recrystallised successively from acetone, alcohol, and chloroform, and then has m. p. 142—142·5°; the mother liquor after fourteen days has deposited a new substance, *ostruthol*, m. p. 134—134·5°, which depresses the m. p. of oxypeucedanin and does not form an additive compound with hydrogen chloride. The benzene-light petroleum solution contains another new substance, *osthol*, m. p. 83—84°, and ostruthin. The last-mentioned substance is better isolated from the rhizome by the alcohol method recommended by Gorup-Besanez and Jassoy.

The percentage yields of these substances are: oxypeucedanin, 1·3; ostruthol, 0·3; osthol, 0·1; ostruthin, 0·5. Young two-year old rhizomes of *Peucedanum*, extracted by the benzene process, yield 2%

of peucedanin and 0·3% of oxypeucedanin, whilst old roots yield 2·5 and 0·5% respectively of the two substances. These figures refute the current view of the formation of the oxypeucedanin, for since the percentage of both peucedanin and oxypeucedanin in old rhizomes is greater than in young roots, the latter cannot be produced by oxidation at the expense of the former. The oxypeucedanin from *Imperatoria* is shown to be identical with that from *Peucedanum* by a mixed m. p. determination and by a comparison of the hydrogen chloride additive compounds.

Being able to obtain oxypeucedanin in comparatively large quantities, the authors have examined its properties more fully than previous investigators. It is optically inactive, and has m. p. 142—142·5°. The analytical data point to the formula $C_{13}H_{12}O_4$, which is confirmed by a determination of the molecular weight in glacial acetic acid and in benzene by the ebullioscopic method. By passing hydrogen chloride into a concentrated alcoholic solution at 0° and then slowly adding a large amount of water, a white, crystalline *substance*, m. p. 155·5—157°, is obtained, the analysis of which points to the formula $C_{36}H_{34}O_{11}Cl_2$, but the authors regard the substance as an additive compound of $C_{13}H_{12}O_4$, the discrepancy being attributed to the ready loss of hydrogen chloride. Boiling 10% sulphuric acid changes oxypeucedanin into an isomeric *substance*, $C_{13}H_{12}O_4$, m. p. 144—145·5°, which does not form an additive compound with hydrogen chloride. By treating oxypeucedanin with boiling 1% oxalic acid, a hydrated *product*, $C_{13}H_{14}O_5$, m. p. 132—133°, is obtained, which forms yellow crystals, and has a molecular weight in boiling glacial acetic acid corresponding with its formula. It readily loses water by treatment with 38% hydrochloric acid, yielding the isomeride of oxypeucedanin, m. p. 144—145·5°, which is also produced by the action of zinc and boiling acetic acid on the hydrogen chloride additive compound of oxypeucedanin. The hydrated product forms a yellow acetyl *derivative*, $C_{15}H_{16}O_6$, m. p. 155·5—156·5°, and a *phenylurethane*, $C_{20}H_{19}O_6N$, m. p. 170—170·5°, from both of which the hydrated product can be regenerated by the action of alcoholic potassium hydroxide and alcoholic ammonia respectively. Oxypeucedanin in acetone is reduced by aluminium amalgam, yielding a mixture which is separable by alcohol; the less soluble constituent, m. p. 203—205°, has a molecular weight in boiling acetic acid corresponding with the formula $(C_{13}H_{13}O_4)_2$, a result suggesting that oxypeucedanin is an unsaturated lactone. This conception is supported by the behaviour of oxypeucedanin with alkali hydroxides; with excess of alkali, it gives in aqueous-alcoholic solution yellow salts, which decompose at the ordinary temperature in neutral or faintly alkaline solution.

The authors confirm Jassoy's formula, $C_{18}H_{20}O_3$, for ostruthin by analysis, by titration with acid and alkali, and by a Zeisel estimation of the *ester*, $C_{18}H_{19}O_3\cdot CO_2Me$, m. p. 64—65°, obtained by the interaction of methyl chloroformate and a strongly cooled solution of an alkali salt of ostruthin.

Osthol, $C_{15}H_{16}O_3$, m. p. 83—84°, forms long, white crystals, and contains one methoxy-group. In alcoholic solution, it yields with

hydrogen chloride an additive *compound*, $C_{15}H_{16}O_3,HCl$, m. p. 99·5—100°. In aqueous alcohol, it behaves with alkali hydroxides very much like oxypeucedanin, its salts in neutral or faintly alkaline solution decomposing into free alkali and osthol, which, therefore, is probably a lactone.

Osthruthol crystallises in white needles, m. p. 134—134·5°, and from the analytical data and the determination of its molecular weight in boiling benzene or methyl alcohol, has the composition $(C_3H_3O)_8$. Its behaviour with alkali hydroxides is similar to that of oxypeucedanin and osthol, the yellow solutions of the salts being decomposed by carbon dioxide. Osthruthol is probably a lactone. C. S.

Rhein. OTTO A. OESTERLE and G. RIAT (*Arch. Pharm.*, 1909, **247**, 527—534).—Rhein, the formula of which now appears to be established beyond doubt as $C_{15}H_8O_6$, yields a dark red, crystalline *potassium* derivative, $C_{15}H_6O_6K_2,9H_2O$, and a *propionate*,

$$C_{15}H_6O_4(O\cdot CO\cdot CH_2\cdot CH_3)_2,$$

m. p. 223—224°.

Farbwerke vorm. Meister, Lucius und Brüning (D.R.-P. 158277) have shown that ethyl chloroacetate reacts easily with anthraquinone derivatives containing hydroxyl groups in the β-position, yielding ethers of ethyl glycollate. When the potassium derivative of rhein is boiled from seventeen to eighteen hours with ethyl chloroacetate, a golden-yellow, crystalline *substance*, $C_{23}H_{20}O_{10}$, m. p. 153—154°, is obtained, containing two ethyl glycollate residues. Since, however, the substance yields an *acetyl* derivative, m. p. 179—180°, in the usual way, the ethyl glycollate groups cannot have entered both the phenolic hydroxyl groups in rhein: one must be present in a hydroxyl group in a side-chain. The authors were proving that this hydroxyl group is present as a carboxyl group when Robinson and Simonsen's paper appeared (Trans., 1909, **95**, 1085), in which rhein is shown to be a dihydroxy-anthraquinonecarboxylic acid. The behaviour of rhein with ethyl chloroacetate is in accordance with the probability that rhein is a derivative of chrysazin (Abstr., 1909, i, 946). C. S.

Chlorophyll. VIII. Degradation of Chlorophyll by Alkalis. RICHARD WILLSTÄTTER and HERMANN FRITZSCHE (*Annalen*, 1910, **371**, 33—124. Compare this vol., ii, 150).—The present investigation on the products formed successively by the action of alkalis on chlorophyll is mainly an amplification of the work of Willstätter and Pfannenstiel on rhodophyllin (compare Abstr., 1908, i, 198). The chlorophylls are derivatives of a tricarboxylic acid; crystalline chlorophyll contains two carbmethoxy-groups, whilst the amorphous compound contains only one carbmethoxy-group and one phytol residue. Crystalline chlorophyll, when hydrolysed, yields a tricarboxylic acid (chlorophyllin), which is acted on by methyl sulphate, yielding the corresponding trimethyl ester, a substance far more soluble than chlorophyll and very similar in composition and properties to the compound formed by the prolonged action of methyl alcohol on chlorophyll. Amorphous chlorophyll, which cannot be obtained

entirely free from impurities, when hydrolysed and subsequently methylated yields a trimethyl ester identical with that derived from crystalline chlorophyll; this ester when treated with potassium hydroxide is converted into the potassium salt of chlorophyllin, identical with the salt prepared directly from crystalline chlorophyll. The various preparations of the trimethyl ester contain two distinct substances: a blue compound and a green compound soluble with difficulty, which are separated by fractional precipitation and are similar in composition.

The action of alkalis on chlorophyll at 100—200° leads to the formation of two dicarboxylic acids, glaucophyllin and rhodophyllin, which are very similar both in chemical and physical properties, and can be separated only by the difference in their acidic properties.

The formation of rhodophyllin at 200° is accompanied by that of a monocarboxylic acid, phyllophyllin, whilst a second monocarboxylic acid, pyrrophyllin, is formed at 225—240°; the two compounds just mentioned are extremely similar, both chemically and optically; phyllophyllin is distinguished, however, by the solubility of the alkali and alkaline earth salts in ether. The monocarboxylic acids are less acidic than the dicarboxylic acids; thus, rhodophyllin may be separated from them by means of dilute ammonium hydroxide, in which phyllophyllin and pyrrophyllin are insoluble.

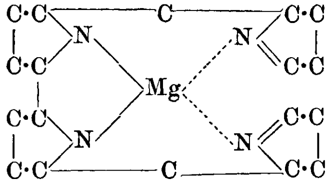
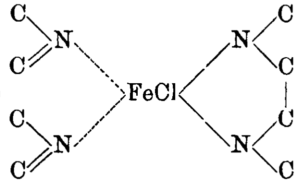
The phyllins are converted by acids into the corresponding porphyrins, compounds which do not contain magnesium. In order to emphasise this relationship between phyllins and porphyrins, it is proposed to change the name of the compound derived from rhodophyllin from *allo*porphyrin into rhodoporphyrin (compare Willstätter and Pfannenstiel, *loc. cit.*).

The dicarboxylic acids, glaucoporphyrin and rhodoporphyrin, are well-defined, crystalline compounds, soluble with difficulty and extremely similar in chemical properties; rhodoporphyrin is not identical with Tschirch's phyllopurpuric acid, as suggested by Marchlewski (compare Abstr., 1908, i, 357). The monocarboxylic porphyrins, phylloporphyrin and pyrroporphyrin, resemble one another so closely that it is difficult to decide which of them corresponds with the substance described hitherto as phylloporphyrin, although it is very probable that the more basic of the two compounds (phylloporphyrin) is identical with the phylloporphyrin described by Marchlewski recently (*loc. cit.*); the phylloporphyrin of previous investigators was undoubtedly contaminated with other porphyrins.

The analysis of the complex substances described in this paper is rendered difficult owing to the stability of the compounds which they form with ether; however, from the results obtained it appears that the complex $[C_{31}H_{34}N_4Mg]$ is common to the phyllins, one, two, and three atoms of hydrogen being replaced by carboxyl in pyrrophyllin and phyllophyllin, glaucophyllin and rhodophyllin, chlorophyll, and the chlorophyllins respectively. The porphyrins are derived from the common nucleus $[C_{31}H_{36}N_4]$ in a similar manner.

As a result of the study of the phyllin esters and salts, particularly of those containing only one carboxyl group, it follows that carboxyl does not take part in the formation of the complex in the derivatives

of chlorophyll, and that only the groups containing nitrogen are available for attachment to the magnesium atom; the centre of the complex may be represented by (I). Applying the same arguments in the case of hæmin, it follows that the iron in hæmin derivatives is combined in the manner indicated by (II) (compare Piloty and Merzbacher, Abstr., 1909, i, 857):

(I.)  (II.) 

I. Phyllins.—Potassium chlorophyllin is a bluish-green powder, analyses of which indicate the atomic proportions N_4:0·90Mg:2·60K; when treated with methyl sulphate, it yields a mixture of two *chlorophyllin trimethyl* esters; the more soluble ester is a bluish-black, microscopic, crystalline powder, whilst the less soluble is a pale green powder. Both esters are decomposed by oxalic acid with the elimination of magnesium and formation of crystalline products containing oxalate; the solutions of the derivatives from the green and blue esters in chloroform are olive-brown and olive-green respectively.

Glaucophyllin, $C_{33}H_{34}O_4N_4Mg$, prepared by the action of a concentrated methyl-alcoholic solution of potassium hydroxide on chlorophyllin under pressure at a temperature not exceeding 140°, is purified by extracting the ethereal solution of the crude material with 0·004% ammonia, treating the aqueous solution with sodium dihydrogen phosphate, extracting with ether, and shaking the ethereal solution with a 0·02—0·05% solution of disodium hydrogen phosphate, in which glaucophyllin is insoluble; it crystallises in small, glistening prisms, which are green by transmitted light and greyish-blue by reflected light, and forms violet-blue solutions with an intense red fluorescence; the *potassium* salt, $C_{31}H_{32}N_4Mg(CO_2K)_2$, crystallises in microscopic, slender, violet prisms. Glaucophyllin is converted by alcoholic potassium hydroxide under pressure at 195—200° into rhodophyllin.

Rhodophyllin forms a complex *potassium* salt,

$$C_{33}H_{32}O_4N_4MgK_2,KOEt;$$

the normal potassium salt when treated with methyl sulphate yields the *dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, which crystallises in glistening prisms with a violet reflex and sinters at 310°.

Pyrrophyllin, $C_{32}H_{34}O_2N_4Mg$, is best prepared by the action of alcoholic potassium hydroxide on rhodophyllin under pressure at 225—230°; it crystallises in tufts of glistening plates, which are steel-blue or greyish-blue with a red tinge; recrystallisation from ether decreases the solubility of the compound without altering the composition; the ethereal solution at the same time changes from blue to red; the substance crystallises from absolute ether in glistening, reddish-violet prisms. The *pyridine* salt crystallises in glistening, violet leaflets; the *potassium* salt, $C_{31}H_{33}N_4Mg{\cdot}CO_2K$, crystallises in short, dark red prisms; the *calcium* salt, $(C_{32}H_{33}O_2N_4Mg)_2Ca$, forms

small, pale red needles; the *ammonium* salt forms brilliant red needles; the *sodium* salt crystallises in pale violet needles.

Phyllophyllin is formed in large quantity by the action of a methyl-alcoholic solution of potassium hydroxide on amorphous chlorophyll under pressure at 225—230°; it has not been isolated in a crystalline form, since it decomposes very readily; the ethereal solution is bluish-red with a red fluorescence; the *caesium* salt, $C_{31}H_{33}N_4Mg\cdot CO_2Cs$, crystallises in compact, glistening, bluish-violet prisms; the *potassium* salt ($1H_2O$) forms glistening, violet prisms; the *calcium* salt crystallises in bright red needles; the *magnesium* salt forms glistening, slender needles.

II. PORPHYRINS.—*Glaucoporphyrin*, $C_{33}H_{36}O_4N_4$, crystallises in reddish-violet, microscopic needles; it sinters at 270° and is completely decomposed at 290—295°; the *potassium* salt,

$$C_{31}H_{34}N_4(CO_2K)_2,4H_2O,$$

crystallises in slender, pale brown leaflets; the *complex salt* with zinc acetate crystallises in glistening, violet prisms.

Rhodoporphyrin forms with zinc acetate an *additive compound*, crystallising in red needles, and with ferric chloride in glacial acetic acid a complex *iron* compound, obtained as a greyish-black, crystalline powder; the *dimethyl* ester, $C_{31}H_{34}N_4(CO_2Me)_2$, crystallises in glistening, reddish-brown prisms with a coppery reflex.

Pyrroporphyrin, $C_{32}H_{36}O_2N_4$, crystallises in dark red, truncated prisms with a violet, metallic reflex; the solution in glacial acetic acid is red with a slight blue tinge. The *hydrochloride*, $C_{32}H_{36}O_2N_4,2HCl$, crystallises in brown, slender, pointed prisms; the *hydrochloride*, $C_{32}H_{36}O_2N_4,3HCl$, forms glistening, rhomboidal leaflets, which are brownish-red by transmitted light, violet by reflected light; the *potassium* salt, $C_{31}H_{35}N_4\cdot CO_2K$, crystallises in reddish-brown prisms and rhomboidal leaflets; the *magnesium* salt was analysed; the *methyl* ester, $C_{31}H_{35}N_4\cdot CO_2Me$, crystallises in long prisms; the *acetyl* compound, $C_{31}H_{35}N_4\cdot CO_2Ac$, prepared by the action of hot acetic anhydride on pyroporphyrin, crystallises in rhomboidal leaflets and long prisms, which are red by transmitted light.

Phylloporphyrin crystallises in dark red, pointed prisms with a violet, metallic reflex; the solution in glacial acetic acid is dark violet-red; the *hydrochloride*, $C_{32}H_{36}O_2N_4,3HCl$, crystallises in glistening, violet, four-sided prisms; the *magnesium* salt, $(C_{32}H_{35}O_2N_4)_2Mg$, is a brownish-red powder. The compound described by Schunck and Marchlewski as a zinc salt is a complex zinc compound.

The absorption spectra of alcoholic and ethereal solutions of glaucophyllin, pyrrophyllin, phyllophyllin, pyrroporphyrin, and phylloporphyrin, and of the hydrochlorides of the last two substances have been measured and are represented graphically. W. H. G.

The Tanning Process. JOHANN VON SCHROEDER (*Kolloidchem. Beihefte*, 1909, 1, 1—57).—The quantity of tannic acid adsorbed by unit weight of hide-powder is approximately constant; the amount which can be washed out again is less the longer the two have remained in contact. Water plays a certain part in the process, for hide-powder takes up no tannin from an alcoholic solution. A preliminary

treatment of the powder with formaldehyde largely prevents the subsequent adsorption of tannic acid. Gelatin resembles hide-powder in its relationship to tannic acid, if due allowance is made for the differences of physical condition of the two former substances under the circumstances of the experiment. G. S. W.

Constitution of Hydroxymethylfurfuraldehyde. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, **6**, 1047—1053. Compare Kiermayer, Abstr., 1896, i, 144; Fenton and Robinson, Trans., 1909, **95**, 1334).—Hydroxymethylfurfuraldehyde is formed by dehydration of chitose, and is the aldehyde, $\begin{matrix} CH{=\!=}C(COH) \\ | \\ CH{:}C(CH_2{\cdot}OH) \end{matrix}\!\!>\!O$, corresponding with 2-hydroxymethylfuran-5-carboxylic acid, not with 4-hydroxy-2-methylfuran-5-carboxylic acid, as supposed by Kiermayer. The small proportion of furfuraldehyde obtained by heating certain pentoses is attributed to the partial decomposition of the hydroxymethylfurfuraldehyde first formed. A. J. W.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. VIII. LUDWIG KALUZA (*Monatsh.*, 1909, **30**, 701—726. Compare Andreasch, Abstr., 1908, i, 683, 684).—Rhodanic acids have been prepared from ψ-cumidine and *iso*hexylamine.

3-ψ-*Cumylrhodanic acid*, $C_6H_2Me_3{\cdot}N{<}\begin{matrix} CS{-}S \\ CO{\cdot}CH_2 \end{matrix}$, is obtained in the form of an oil from the corresponding ester, *ethyl* ψ-*cumyldithiocarbamacetate*, $C_6H_2Me_3{\cdot}NH{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2Et$, which is formed by the interaction of ethyl chloroacetate and ammonium cumyldithiocarbamate, and crystallises in short, transparent prisms, m. p. 84°.

5-*Benzylidene*-3-ψ-*cumylrhodanic acid*,

$$C_6H_2Me_3{\cdot}N{<}\begin{matrix} CS{-}S \\ CO{\cdot}C{:}CHPh \end{matrix},$$

prepared by condensation with benzaldehyde, is a citron-yellow oil, crystallising in citron-yellow needles, m. p. 127°.

5-mp-*Methylenedioxybenzylidene*-3-ψ-*cumylrhodanic acid*, similarly prepared by condensation with piperonal, is a coarse, chrome-yellow powder, consisting of prismatic needles, m. p. 188°.

5-m-*Nitrobenzylidene*-3-ψ-*cumylrhodanic acid* forms a sulphur-yellow, crystalline powder, m. p. 224°. The corresponding 5-p-*nitrobenzylidene*-3-ψ-*cumylrhodanic acid* is a dark yellow powder, which becomes brown at 190°, sinters at 200°, m. p. 230°.

5-p-*Dimethylaminobenzylidene*-3-ψ-*cumylrhodanic acid* forms splendid blood-red, stout needles, m. p. 192°. The alcoholic solution is a deep chrome-yellow when dilute, blood-red when concentrated.

5-p-*Methoxybenzylidene*-3-ψ-*cumylrhodanic acid* forms glistening, chrome-yellow, microscopic prisms, m. p. 174°.

iso*Hexylamine* iso*hexyldithiocarbamate*, $C_6H_{13}{\cdot}NH{\cdot}CS{\cdot}S{\cdot}NH_3{\cdot}C_6H_{13}$, prepared by the interaction of *iso*hexylamine and carbon disulphide, forms colourless, regular, prismatic crystals, m. p. 85°. It reacts with ethyl monochloroacetate, forming 3-iso*hexylrhodanic acid*,

$$C_6H_{13}{\cdot}N{<}\begin{matrix} CS{-}S \\ CO{\cdot}CH_2 \end{matrix},$$

a clear, fluid, transparent, light yellow oil, b. p. 199—200°/11 mm.

5-*Benzylidene*-3-iso*hexylrhodanic acid*, $C_6H_{13}\cdot N<\begin{array}{l}CS-S\\ CO\cdot C:CHPh\end{array}$, forms long, lustrous, bright yellow needles, m. p. 87°. 5-m-*Nitrobenzylidene*-3-iso*hexylrhodanic acid* crystallises in light yellow, glistening plates, m. p. 166—167°. 5-p-*Nitrobenzylidene*-3-iso*hexylrhodanic acid* is a brownish-yellow, microcrystalline powder, m. p. 130—131°.

5-mp-*Methylenedioxybenzylidene*-3-iso*hexylrhodanic acid*,

$$C_6H_{13}\cdot N<\begin{array}{l}CS-S\\ CO\cdot C:CH\cdot C_6H_3<\begin{array}{c}O\\ O\end{array}>CH_2\end{array},$$

consists of golden-yellow, lustrous needles with a blue reflex, m. p. 98°. 5-p-*Dimethylaminobenzylidene*-3-iso*hexylrhodanic acid* forms a matted mass of lustrous, red needles with a blue reflex, m. p. 140°. 5-o-*Hydroxybenzylidene*-3-iso*hexylrhodanic acid* crystallises in orange-yellow, short, matted needles, m. p. 170—172°. With sodium hydroxide, bluish-red crystals of the sodium salt are formed. It dyes wool and silk bright yellow.

5-p-*Methoxybenzylidene*-3-iso*hexylrhodanic acid* forms long, chrome-yellow, lustrous needles, m. p. 85°.

5-*Cinnamylene*-3-iso*hexylrhodanic acid* forms golden, crystalline masses, consisting of regular, rectangular, microscopic cubes, m. p. 129—131°.

iso*Hexylthiocarbimide*, $SC:N\cdot[CH_2]_3\cdot CHMe_2$, prepared by the interaction of ethyl chlorocarbamate and *iso*hexylamine *iso*hexyldithiocarbamate, is a faintly yellow-coloured, clear, mobile oil, with a not unpleasant odour, b. p. 120—121°/18 mm., 208—209°/760 mm. When treated with ammonia and alcohol, iso*hexylthiocarbamide*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_{13},$$

is formed, crystallising in thin, rectangular plates, m. p. 62°, of fatty lustre. *Di*iso*hexylthiocarbamide*, $CS(NH\cdot C_6H_{13})_2$, forms thin, silvery-glistening, rhombic plates, m. p. 46°.

iso*Hexylthioparabanic acid*, $CS<\begin{array}{l}N(C_6H_{13})\cdot CO\\ NH\text{——}CO\end{array}$, prepared by the interaction of *iso*hexylthiocarbamide and cyanogen, crystallises in light yellow, thin plates, m. p. 110°. By the action of silver nitrate it is converted into iso*hexylparabanic acid*, $CO<\begin{array}{l}N(C_6H_{13})\cdot CO\\ NH\text{——}CO\end{array}$, which forms long, colourless, silky, matted needles, m. p. 76°. *Di*iso*hexylthioparabanic acid* crystallises in long, flat, citron-yellow needles, m. p. 40°. *Di*iso*hexylparabanic acid* was only obtained in the form of a syrup. E. F. A.

Additive Products of Halogen Acetamide with Atropine.

ALFRED EINHORN and MAXIMILIAN GÖTTLER (*Ber.*, 1909, 42, 4853—4854).—The additive product of atropine with bromoacetonitrile has been shown by Braun (Abstr., 1908, i, 675) to have lost the specific pharmacological action of atropine; this is not, however, the case as regards the compounds with the halogen acetamides.

Atropinechloroacetamide forms a flocculent precipitate of lustrous

plates, m. p. 204—205° (decomp.). *Atropinebromoacetamide* forms bunches of matted needles, m. p. 204—205°; *atropineiodoacetamide* forms an indefinitely crystalline aggregate, m. p. 203—204° (decomp.).

E. F. A.

Caffeine. A. J. ULTÉE (*Chem. Weekblad*, 1910, **7**, 32—34).—Additive products of caffeine with pyrogallol and phloroglucinol respectively have been prepared; they contain equimolecular proportions of their constituents. *Caffeine-pyrogallol*, $C_8H_{10}O_2N_4,C_6H_6O_3,4H_2O$, forms acicular crystals, m. p. 70°. The water of crystallisation is given off in a vacuum desiccator over sulphuric acid. The whole of the caffeine can be extracted by chloroform.

Caffeine-phloroglucinol, $C_8H_{10}O_2N_4,C_6H_6O_3,2H_2O$, forms ill-defined crystals, m. p. about 185°.

Theobromine is rapidly converted into caffeine by the action of methyl sulphate.

A. J. W.

Action of Grignard's Solutions on β-Cinchonine- and β-Quinine-ethiodides. MARTIN FREUND and FRITZ MAYER (*Ber*, 1909, **42**, 4724—4728).—The β-ethiodide of cinchonine (Skraup and Norwall, Abstr., 1894, i, 391) has a constitution analogous to that of quinoline methiodide, and reacts with Grignard's reagent in much the same manner, yielding 1 : 2-diethyl-1 : 2-dihydrocinchonine and 2-phenyl-1-ethyl-1:2-dihydrocinchonine, $C_6H_4<\begin{matrix}\text{———}C(C_{10}H_{16}ON)\\NEt\cdot CHEt(or\ Ph)\end{matrix}>CH$. Quinine β-methiodide reacts in the same manner.

1 : 2-*Diethyl*-1 : 2-*dihydrocinchonine*, $C_{23}H_{32}ON_2$, crystallises from alcohol in needles, which sinter at 173° and are completely molten at 187°. Its salts do not crystallise, and the yield of the base is poor.

2-*Phenyl*-1-*ethyl*-1 : 2-*dihydrocinchonine*, $C_{27}H_{32}ON_2$, crystallises from dilute alcohol in slender needles, and has m. p. 135° after softening at 120°. The *hydriodide*, $C_{27}H_{32}ON_2,HI$, crystallises in plates, which decompose at 263°. The corresponding *hydrochloride* and *hydrobromide* have been prepared.

The *product* $C_{24}H_{34}O_2N_2$, obtained from quinine-β-ethiodide and ethyl magnesium bromide, could not be obtained in a crystalline form. The physiological properties of the products have been studied.

J. J. S.

Action of Chloroform on 2 : 5-Dimethylpyrrole. GIUSEPPE PLANCHER and U. PONTI (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 469—474).—The action of chloroform on 2 : 5-dimethylpyrrole in presence of alcoholic potassium hydroxide yields 2 : 5-dimethylpyrrole-3-aldehyde, 2-(or 3-)dichloromethyl-2 : 5-dimethylpyrrolenine, and 3-chloro-2 : 6-dimethylpyridine (compare Bocchi, Abstr., 1900, i, 357).

2 : 5-*Dimethylpyrrole*-3-*aldehyde*, $NH<\begin{matrix}CMe:C\cdot CHO\\ \quad\ \ |\\CMe:CH\end{matrix}$, forms colourless scales or mammillary crystals, m. p. 144°, and does not reduce Fehling's solution. Its p-*nitrophenylhydrazone*, $C_{13}H_{14}O_2N_4$ forms garnet-red crystals with metallic lustre, m. p. 234°. With

β-naphthylamine (1 mol.) and pyruvic acid (1 mol.) in alcoholic solution, the aldehyde (1 mol.) gives the corresponding *naphthacinchoninic acid*, m. p. 267°.

2 : 5-*Dimethyl-(?)-dichloromethylpyrrolenine*, $N\Big\langle\begin{array}{l}CMe\text{------}CH \\ CMe(CHCl_2)\cdot CH\end{array}$ or $N\Big\langle\begin{array}{l}CMe{:}CH \\ CMe\cdot CH\cdot CHCl_2\end{array}$, is a heavy, colourless liquid having a basic odour resembling that of burnt almonds, and yields a *picrate*,

$$C_7H_9NCl_2,C_6H_3O_7N_3,$$

separating in pale yellow, rhombic scales, m. p. 144°. T. H. P.

Constitution of Hæmopyrrole and of Hæmopyrrolecarboxylic Acid. OSCAR PILOTY and E. QUITMANN (*Ber.*, 1909, **42**, 4693—4703).—Pure hæmopyrrole can be obtained by carefully fractionating the crude product prepared by the method described previously (Abstr., 1909, i, 539). It has b. p. 114—115°/35 mm., m. p. 39°, and forms flat, quadratic plates. When fused, it forms a colourless oil with a pale fluorescence. The potassium derivative forms a colourless, crystalline powder, and the picrate has m. p. 108·5°. The constitution of hæmopyrrole has been settled by the action of nitrous acid. 2 : 4-Dimethylpyrrole (Knorr, Abstr., 1884, 1368), when treated with nitrous acid, yields the oxime of citraconimide, the 2-methyl group being eliminated. Pure hæmopyrrole and nitrous acid yield the oxime of methylethylmaleinimide, and as in this reaction a 2-methyl group is probably eliminated, hæmopyrrole should be a dimethylethylpyrrole :

$$NH\Big\langle\begin{array}{l}CMe{:}CMe \\ CH{=}CEt\end{array} \quad\text{or}\quad NH\Big\langle\begin{array}{l}CH{=}CMe \\ CMe{:}CEt\end{array}$$

2 : 5-Dimethylpyrrole (Paal, Abstr., 1885, 1206 ; Knorr, *ibid.*, 995) and nitrous acid yield the dioxime of dimethyltetraketone,

$$COMe\cdot C({:}N\cdot OH)\cdot C({:}N\cdot OH)\cdot COMe$$

(compare Thal, Abstr., 1892, 1074).

Methylethylmaleinimidemonoxime,

$$NH\Big\langle\begin{array}{l}C({:}N\cdot OH)\cdot CMe \\ CO\text{--------}CEt\end{array} \quad\text{or}\quad NH\Big\langle\begin{array}{l}CO\text{--------}CMe \\ C({:}N\cdot OH)\cdot CEt\end{array},$$

crystallises from water in colourless prisms, and has m. p. 201°. It is identical with the compound described previously (Abstr., 1909, i, 539) as melting at 206—207°. When hydrolysed with dilute sulphuric acid it yields methylethylmaleinimide.

Citraconimidemonoxime, $NH\Big\langle\begin{array}{l}CO\text{--------}CMe \\ C({:}NOH)\cdot CH\end{array}$, forms small, colourless prisms, m. p. 223—224°, and when hydrolysed yields citraconic acid.

The oxime of hæmatic acid (*loc. cit.*, 540) when hydrolysed yields hæmatic acid.

It has not been found possible to decompose hæmopyrrole by means of hydroxylamine, although both 2 : 4- and 2 : 5-dimethylpyrroles are decomposed by this reagent (Ciamician and Zanetti, Abstr., 1890, 264, 1155).

A number of products are formed by reducing hæmatoporphyrin

with hydriodic acid and phosphorus; among these is an oil of low b. p., which yields a *picrate*, $C_{14}H_{18}O_7N_3$, m. p. 143—145°.

J. J. S.

New Cinchonic Acid Syntheses. ROBERT SCHIFF (*Ber.*, 1909, 42, 4918. Compare Borsche, Abstr., 1909, i, 955).—A claim for priority.

R. V. S.

Quinoline Derivatives. ALFRED EINHORN (*Ber.*, 1909, 42, 4854—4856).—[With RICHARD FEIBELMANN.]—*Ethyl quinoline*-6-*carboxylate hydrochloride* is prepared by boiling a suspension of the hydrochloride of *p*-quinolinecarboxylic acid in alcohol containing hydrogen chloride; it crystallises in bunches of needles, m. p. 210° (decomp.). The free acid forms matted needles, m. p. 50°.

The *hydrochloride* of *diethylaminoethyl quinoline*-6-*carboxylate*,

$$C_9H_6N\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot NEt_2,HCl,$$

prepared by the action of diethylaminoethanol on quinoline-6-carboxylic acid, is a faintly yellow-coloured, microcrystalline substance, m. p. 180°.

[With MAXIMILIAN GÖTTLER.]—*Quinolineiodoacetamide*,

$$C_9NH_7I\cdot CH_2\cdot CO\cdot NH_2$$

crystallises from water in lustrous, orange-hued, refractive plates, or from alcohol in yellow needles, decomp. 250°; the solution has a green fluorescence.

E. F. A.

Action of Magnesium *cyclo*Hexyl Bromide on Tetramethyldiaminobenzophenone. ANDRÉ WAHL and ANDRÉ MEYER (*Bull. Soc. chim.*, 1910, [iv], 7, 28—31. Compare Abstr., 1908, i, 890).—The authors have repeated the experiments of Schmidlin and Escher (Abstr., 1908, i, 163), and have succeeded in obtaining a small quantity of cyclo*hexylidenetetramethyldiaminodiphenylmethane*,

$$C_6H_{10}\colon C(C_6H_4\cdot NMe_2)_2,$$

m. p. 144—145°.

This was obtained by treating an ethereal solution of magnesium *cyclo*hexyl bromide with tetramethyldiaminobenzophenone and adding water. The precipitate, after the removal of magnesium compounds, consists mainly of unaltered ketone, from which the substance sought was separated by tedious fractionation from solutions in a mixture of acetone and ether, in which it is readily soluble. It crystallises in bright yellow prisms, and when dissolved in acetic acid gives with mild oxidising agents, such as lead peroxide, an intensely blue coloration, resembling that similarly obtained by Lemoult (Abstr., 1909, i, 836) with the *pp*-dialkyl derivatives of *as*-diphenylethylene. Since this new substance gives this reaction, it follows that the development of this blue dye is not due, as Lemoult supposed, to the specific influence of a characteristic hydrogen atom, since this is absent in the new substance.

T. A. H.

Reaction of Nitrosoamides with Phenylhydrazine. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1909, 42, 4872—4877).—When nitrosoformanilide reacts with phenylhydrazine (more than 2 mols.) in benzene at 0°, nitrogen is evolved and *s*-formylphenyl-

hydrazide is produced. This is not an instance of the migration of an acyl group, because nitrosoformo-*p*-toluidide and phenylhydrazine also yield *s*-formylphenylhydrazide, and nitrosoformanilide and *p*-tolylhydrazine yield *s*-formyl-*p*-tolylhydrazide. The reaction consists, therefore, in an acylation of the hydrazine by the nitrosoacylamide, which thus is converted into a diazo-compound; this, reacting with a second molecule of the hydrazine, forms a diazohydrazide, by the decomposition of which nitrogen and an aromatic hydrocarbon are produced:

(1) $CHO{\cdot}NPh{\cdot}NO + NHPh{\cdot}NH_2 = NHPh{\cdot}NH{\cdot}CHO + PhN_2{\cdot}OH$.
(2) $PhN_2{\cdot}OH + NHPh{\cdot}NH_2 = NH_2{\cdot}NPh{\cdot}N_2Ph + H_2O$.
(3) $NH_2{\cdot}NPh{\cdot}N_2Ph = 2C_6H_6 + 2N_2$.

The diazohydrazides can be isolated under suitable conditions. Nitrosoformanilide is very slowly introduced into a well-cooled dilute benzene solution of phenylhydrazine, the formylphenylhydrazine is removed, and the last portions are precipitated by the addition of light petroleum; the filtrate is evaporated, whereby a residue of diazobenzenephenylhydrazide, m. p. 71°, is obtained.

In a similar way, phenylhydrazine reacts with nitrosoacetanilide, nitrosophenylcarbamide, and nitrosomethylurethane, forming *s*-acetylphenylhydrazide, phenylsemicarbazide, and ethyl phenylcarbazinate respectively.

Other nitroso-compounds lose their nitroso-group by treatment with phenylhydrazine; nitrosophenylurethane, nitrosobenzanilide, diphenylnitrosoamine, and phenylethylnitrosoamine are converted into phenylurethane, benzanilide, diphenylamine, and phenylethylamine respectively; nitrous oxide is evolved in the last two cases.

Nitrosoformanilide and aniline in alcohol solution yield diazoaminobenzene and formanilide, the reaction following a course similar to the first-mentioned above. C. S.

New Phototropic Substances. II. MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 559—564. Compare Abstr., 1909, i, 964).—The authors have obtained the following further results:

Cinnamaldehydephenylhydrazone, m. p. 171° (Fischer, Abstr., 1884, 1150, found 168°), is slightly phototropic.

Piperonaldehydephenylhydrazone, m. p. 106° (Rudolph, Abstr., 1889, 251, found 102—103°), is not phototropic.

p-*Tolualdehydephenylhydrazone*, $NHPh{\cdot}N{:}CH{\cdot}C_6H_4Me$, forms a yellow, crystalline powder, m. p. 121°, and is feebly phototropic.

With the *m*-tolylhydrazones, phototropy is observed, but less frequently and less intensely than with the *p*-tolylhydrazones; the corresponding ortho-compounds are not phototropic.

*Benzaldehyde-*m*-tolyhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CHPh$, separates in slender, whitish-yellow needles, m. p. 100°, and exhibits phototropic properties.

*Anisaldehyde-*m*-tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}OMe$, forms a yellow, crystalline powder, m. p. 111°, and is not phototropic.

*Cuminaldehyde-*m*-tolylhydrazone*, $C_6H_4Me{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}CHMe_2$, crystallises in yellowish-white needles, m. p. 136°, and is faintly phototropic.

Cinnamaldehyde-m-*tolylhydrazone*, $C_6H_4Me\cdot N_2H:CH\cdot CH:CHPh$, forms a yellow, crystalline powder, m. p. 131°, and is feebly phototropic.

Piperonaldehyde-m-*tolylhydrazone*, $C_6H_4Me\cdot N_2H:CH\cdot C_6H_3:O_2:CH_2$, forms canary-yellow needles, m. p. 131°, and is distinctly phototropic.

p-*Tolualdehyde*-m-*tolylhydrazone*, $C_6H_4Me\cdot N_2H:CH\cdot C_6H_4Me$, separates as an intensely yellow, crystalline powder, m. p. 121°, and is not phototropic.

Benzaldehyde-*o*-tolylhydrazone becomes coloured in the air even in the dark, but much more slowly than is the case with a phototropic compound (compare Reutt and Pawlewski, Abstr., 1904, i, 99). Such coloration appears to be favoured by moisture.

Anisaldehyde-o-*tolylhydrazone* crystallises in shining, white scales, m. p. 94°, and is not phototropic, but it softens in the air, giving ultimately a dark red syrup.

Cuminaldehyde-o-*tolylhydrazone* forms canary-yellow, shining scales, m. p. 91°, and is not phototropic; it readily changes in the air, its colour becoming red and its m. p. being lowered.

Piperonaldehyde-o-*tolylhydrazone* forms shining, yellow scales, m. p. 87°, and is not phototropic.

p-*Tolualdehyde*-o-*tolylhydrazone* crystallises in pale yellow scales, m. p. 109°, and is not phototropic; it readily becomes red in the air, especially in moist air. T. H. P.

Synthesis of Polypeptides. XXXII. Derivatives of *l*-Proline and of Phenylalanine. EMIL FISCHER and ANDREAS LUNIAK (*Ber.*, 1909, 42, 4752—4759. Compare Fischer and Suzuki, Abstr., 1904, i, 771; Fischer and Reif, *ibid.*, 1908, i, 1007).—l-*Prolyl*-l-*phenylalanine*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2-NH\end{matrix}>CH\cdot CO\cdot NH\cdot CH<\begin{matrix}CO_2H\\ CH_2Ph\end{matrix}$, prepared by condensing *l*-prolyl chloride with *l*-phenylalanine ethyl ester and hydrolysing the resulting product with barium hydroxide, is identical with the dipeptide obtained by Osborne and Clapp (Abstr., 1908, i, 115) by the hydrolysis of gliadin with sulphuric acid.

The dipeptide is decomposed by pancreatin in a sodium carbonate solution at 36° during the course of forty-eight hours, and yields *l*-proline and *l*-phenylalanine.

l-*Prolyl*-d-*phenylalanine*, $C_{14}H_{18}O_3N_2,H_2O$, has also been prepared synthetically; it forms small, colourless prisms, has m. p. 223° (corr., decomp.), is more soluble in water than the isomeride, and has a bitter taste.

The *copper* salt, $C_{14}H_{16}O_3N_2Cu,2H_2O$, forms dark blue, microscopic prisms. J. J. S.

Aminopyrrolidone Derivatives from Mesityl Oxide and Aminolactones from Diacetone Alcohol. MORITZ KOHN and FRIEDRICH BUM (*Monatsh.*, 1909, 30, 729—743. Compare Abstr., 1908, i, 819, 829).—A continuation of previous work. The 4-methylamino-1:2:2:4-dimethyl-5-pyrrolidone, $C_9H_{18}ON_2$, is now obtained as a colourless, crystalline mass, m. p. 32°, b. p. 121—122°/11 mm.

It reacts with ethylene oxide, forming a colourless, amorphous *compound*, $CMe_2<\begin{matrix}NMe\cdot CO \\ CH_2-CMe\cdot NMe\cdot CH_2\cdot CH_2\cdot OH\end{matrix}$; this yields a characteristic *aurichloride*, $C_{11}H_{22}O_2N_2,2HAuCl_4+H_2O$, decomp. 167°. The compound forms an additive *product* with methyl iodide, which was converted into the *methochloride* and analysed as the *platinichloride*, $C_{11}H_{22}O_2N_2,HCl,CH_3Cl,PtCl_4$, which crystallises in orange tablets.

4-*Ethylamino*-2 : 2 : 3-*trimethyl*-1-*ethyl*-5-*pyrrolidone*, $C_{11}H_{22}ON_2$, is a viscid oil, b. p. 127—131°/13—14 mm. The *compound* formed on interaction with ethylene oxide did not crystallise or yield crystalline salts, but was analysed in the form of the *platinichloride* of the *methochloride*, $C_{13}H_{26}O_2N_2,HCl,CH_3Cl,PtCl_4$.

4-Amino-5-keto-2 : 2 : 4-trimethyltetrahydrofuran forms a yellow *picrate*, m. p. 145—146°. The *picrate* of the corresponding 4-methylamino-compound crystallises in orange-yellow needles, m. p. 179°. The corresponding 4-dimethylamino-compound has b. p. 111°/11 mm., and yields a *picrate*, m. p. 175°, crystallising in well-formed citron-yellow needles.

4-*Ethylamino*-5-*keto*-2 : 2 : 4-*trimethyltetrahydrofuran*, synthesised from diacetone alcohol, ethylamine hydrochloride, and potassium cyanide, is a colourless, mobile liquid, b. p. 138—140°/15 mm. The *phenylcarbamide*, $C_{16}H_{22}O_2N_2S$, forms a colourless, sandy powder, m. p. 168°. The lactone further interacts with nitrous acid, forming a *nitroso*-derivative, $CMe_2<\begin{matrix}O——CO \\ CH_2\cdot CMe\cdot N(NO)C_2H_5\end{matrix}$, which crystallises in colourless needles, m. p. 67°. E. F. A.

Action of Formaldehyde and Secondary Bases on Isatin.

ALFRED EINHORN and MAXIMILIAN GÖTTLER (*Ber.*, 1909, **42**, 4850—4852).—By the action of formaldehyde and secondary bases on isatin, two molecules of water are eliminated and condensation products formed, which are considered to be derived from the lactam formula: $CO<\begin{matrix}CO \\ C_6H_4\end{matrix}>N\cdot CH_2\cdot NRR'$.

ω-*Diethylaminomethylisatin* forms short, red crystals, aggregated in large clusters, m. p. 77—78°. ω-*Phenylethylaminomethylisatin* crystallises in deep red, reniform aggregates of thin plates, m. p. 98°.

E. F. A.

Synthesis of 5 : 7 : 5′ : 7′-Tetrabromoindigotin and 5 : 7 : 5′ : 7′-Tetrachloroindigotin.

NEGOÏTA DANAÏLA (*Compt. rend.*, 1909, **149**, 1383—1385. Compare Abstr., 1908, i, 468, 798).—The constitution of the tetrahalogen derivatives of indigotin follows from the synthesis of these compounds by the reduction of 5 : 7-dibromoisatin chloride and 5 : 7-dichloroisatin chloride with hydrogen iodide (compare Grandmougin, this vol., i, 74).

Details of the absorption spectra of the compounds are given.

W. O. W.

Constitution of Indirubin. LOUIS C. MAILLARD (*Bull. Soc. chim.*, 1909, [iv], 5, 1153—1158).—In a previous paper (Abstr., 1902, i, 371) the author has shown that indigotin dissolved in chloroform to which hydrochloric acid has been added, slowly passes into indirubin, and on this ground has suggested (Abstr., 1903, i, 761) new formulæ for indigotin and indirubin, in which these are represented as polymerides, $C_{32}H_{20}O_4N_4$, of a supposed hemi-indigotin, $C_{16}H_{10}O_2N_2$. The evidence brought forward by Beckmann and Gabel (Abstr., 1906, i, 900) and Vaubel (*ibid.*, 989) that indigotin has the formula $C_{16}H_{10}O_2N_2$ is discounted by the fact that it was not obtained by physical determinations, but this objection does not apply to that derived from Wahl and Bagard's new synthesis of indirubin (Abstr., 1909, i, 300), which, in the opinion of these authors, supports the simple formula generally accepted for this substance. In this connexion the author points out that this acceptance implies (1) that mere standing of indigotin in acidified chloroform is sufficient to rotate the pyrrole nucleus from the α- to the β-position, or (2) that throughout the course of the new synthesis the oxindole nucleus does not remain unchanged in position.

T. A. H.

3-Hydroxyindazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1909, **149**, 1135—1137. Compare Abstr., 1906, i, 544; 1907, i, 158; 1909, i, 145).—*o*-Benzeneazobenzoic acid is obtained in 70—80% yield by condensing *o*-nitrosobenzoic acid with aniline. By treating this with phosphorus pentachloride and oxidising the product, a mixture of *o*-benzeneazochlorobenzoic acids is obtained, which, on treatment with phosphorus pentachloride, yields only 4 : 6-dichloro-3-hydroxyindazole, m. p. 187°. By treating *o*-benzeneazo-*p*-chlorobenzoic acid in the same way, *trichloro-3-hydroxyindazole*,

$$C_6H_2Cl{<}\begin{matrix}N\text{———}\\ |\\ C(OH)\end{matrix}{>}N{\cdot}C_6H_4Cl,$$

has been prepared; it forms needles, m. p. 209—210°.

The formation of a mixture of monochloro-derivatives when phosphorus pentachloride acts on *o*-carboxylic azo-compounds appears to indicate that the formation of chlorohydroxyindazoles is not due to direct chlorination. *Azoxybenzene-o-carboxylic acid*, prepared by condensing phenylhydroxylamine with *o*-nitrosobenzoic acid, crystallises in yellow prisms, m. p. 118°.

Hubner's 3 : 5-dibromoanthranilic acid does not condense with nitrobenzene. The *acetyl* derivative of the acid has m. p. 221° (decomp.); the *methyl* ester forms spangles, m. p. 91°. W. O. W.

Pyrimidines. XLIX. Thio-derivatives of Thymine and the Preparation of Thymine. HENRY L. WHEELER and DAVID F. MCFARLAND [and, in part, WALTER F. STOREY] (*Amer. Chem. J.*, 1910, **43**, 19—36).—Wheeler and Liddle (Abstr., 1909, i, 60) have shown that in the preparation of uracil a larger yield is obtained by condensing ethyl sodioformylacetate with thiocarbamide than by condensing it with ψ-ethylthiocarbamide. Experiments have therefore been carried out in order to ascertain whether the preparation of thymine could be improved in a similar manner. It has been found that when ethyl

sodioformylpropionate is condensed with thiocarbamide in aqueous solution, the yield of 2-thiothymine is only about one-half of that obtained by the use of ψ-ethylthiocarbamide, but that if the reaction is carried out in alcoholic solution, a much larger yield is obtained, amounting to about 22·6% of the calculated quantity, and nearly identical with that furnished by the ψ-ethylthiocarbamide condensation.

2-*Thiothymine*, $NH<\begin{matrix}CS-NH\\CO\cdot CMe\end{matrix}>CH$, forms fairly stout prisms, is soluble in water at 20° to the extent of 0·133%, and is readily converted into thymine by heating its aqueous solution with chloroacetic acid. Thymine is soluble in water at 23° to the extent of 0·303%. 2-Thiothymine has a more pronounced acid character than thymine; its *sodium*, *potassium*, and *copper* salts are described.

2-*Benzylthiol*-5-*methyl*-6-*pyrimidone*, $NH<\begin{matrix}C(S\cdot CH_2Ph)\!:\!N\\CO\text{———}CMe\end{matrix}>CH$, m. p. 204—205°, obtained by the action of benzyl chloride on the potassium salt of 2-thiothymine, forms colourless needles.

6-*Thio*-2-*ethylthiol*-5-*methylpyrimidine*, $NH<\begin{matrix}C(SEt)\!:\!N\\CS-CMe\end{matrix}>CH$, m. p. 181°, obtained by warming 6-chloro-2-ethylthiol-5-methylpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 624) with a solution of potassium hydrogen sulphide, crystallises in prismatic needles, and, when heated at 215° in a current of hydrogen chloride, is converted into 2 : 6-*dithiothymine*, $NH<\begin{matrix}CS\cdot NH\\CS\cdot CMe\end{matrix}>CH$, m. p. 281° (decomp.), which forms small, bright yellow needles.

When 6-thio-2-ethylthiol-5-methylpyrimidine is boiled with concentrated hydrochloric acid for one and a-half hours, it is converted into thymine, but, on less vigorous treatment, 6-*thiothymine*,

$$NH<\begin{matrix}CO\cdot NH\\CS\cdot CMe\end{matrix}>CH,$$

m. p. 330° (decomp.), is produced, which forms bright yellow, silky needles. By the action of methyl iodide on 6-thiothymine in presence of potassium hydroxide, 6-*methylthiol*-5-*methyl*-2-*pyrimidone*,

$$N\leqslant\begin{matrix}CO\text{———}NH\\C(SMe)\cdot CMe\end{matrix}>CH,$$

m. p. 205—211°, is obtained, which forms pale yellow, prismatic needles. When this substance is heated with methyl iodide in presence of potassium hydroxide, 6-*methylthiol*-3 : 5-*dimethyl*-2-*pyrimidone*,

$$N\leqslant\begin{matrix}CO\text{——}NMe\\C(SMe)\cdot CMe\end{matrix}>CH,$$

m. p. 83°, is obtained, which forms white, prismatic needles, and, when boiled with concentrated hydrochloric acid, is converted into 3-methylthymine (Johnson and Clapp, Abstr., 1908, i, 835). E. G.

Derivatives of Piperazine. ANTOINE P. N. FRANCHIMONT and E. KRAMER (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 452—454).—Van Dorp (Abstr., 1909, i, 327), who prepared piperazinediacetic acid together with the corresponding diamide and dinitrile, failed to esterify the acid; this has now been effected. The acid forms a compound with sulphuric acid, and when this is heated with excess of

this acid and alcohol, the crystalline compound of sulphuric acid with the ester is obtained. The ester is freed by treatment with bases under a layer of ether or benzene. The *methyl* ester is a colourless substance, m. p. 63°; the *ethyl* ester, m. p. 47·5°, is also crystalline. Being tertiary amines, both not only combine with acids, but also with methyl iodide, but of this they only unite with one molecule. The compound obtained in this way from the methyl ester has m. p. 144—145°, that from the ethyl ester, m. p. 143°. The compound *piperazinediethylenediamine*,

$$NH_2\cdot CH_2\cdot CH_2\cdot N{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}N\cdot CH_2\cdot CH_2\cdot NH_2,$$

was obtained by reduction of the dinitrile by means of sodium and alcohol. The anhydrous compound, m. p. 40—41°, is hygroscopic, yields with water a crystalline compound, m. p. 63°, and with 4HCl a non-hygroscopic, crystalline *hydrochloride*. The *picrate* and *oxalate* form yellow and colourless crystals respectively; the *picryl* derivative is crystalline and decomposes at 238°, and a *benzoyl* derivative was obtained. Similar derivatives of the lower homologue of the above, namely, *piperazinedimethylenediamine*, were prepared. This compound could not be obtained from the acetamide by Hoffmann's method, so that it was necessary to resort to the sodium and alcohol reduction of *piperazinediformonitrile*. This substance, prepared from bromocyanogen and piperazine in aqueous solution with addition of alkali, crystallises in leaflets, m. p. 168°, and combines neither with methyl iodide, benzene, nor oxalic acid. G. S. W.

Ketochlorides and Quinones of Heterocyclic Compounds and Their Transformation Products. III. Ketochlorides and Quinones of Phenyl-ψ-aziminobenzene [2 : 1 : 3-Benztriazole]. THEODOR ZINCKE and E. SCHARFF (*Annalen*, 1909, **370**, 297—314).—A preliminary note of this investigation has appeared already (compare Zincke and Petermann, Abstr., 1899, i, 135). A complete parallelism is shown to exist between phenyl-ψ-aziminobenzene [2 : 1 : 3-benztriazole] and phenylaziminobenzene [1 : 2 : 3-benztriazole], the different structure of the nitrogen ring having no marked influence on the chemical properties (compare Zincke, Stoffel, and Petermann, Abstr., 1900, i, 524; Zincke and Petermann, Abstr., 1901, i, 104).

5-Amino-2-phenyl-2 : 1 : 3-benztriazole has m. p. 183° (compare Kehrmann and Messinger, Abstr., 1892, 889); the *sulphate* and *hydrochloride* crystallise in colourless needles; the *acetyl* derivative, $C_{14}H_{12}ON_4$, crystallises in faintly pink, silky, slender needles, m. p. 192°.

6-*Chloro*-5-*nitro*-2-*phenyl*-2 : 1 : 3-*benztriazole*, $NPh{<}{N\cdot C:CH\cdot C\cdot NO_2 \atop N\cdot C:CH\cdot CCl}$, is prepared by boiling a solution of 1 : 3-dichloro-4 : 6-dinitrobenzene in 96% alcohol with phenylhydrazine and crystalline sodium acetate; it forms pale yellow needles, m. p. 196°, and when reduced with hydrochloric acid and tin yields the corresponding *amino*-compound, $C_{12}H_9N_4Cl$, small, glistening, brownish-yellow leaflets and needles,

m. p. 221—222°, the *acetyl* derivative of which crystallises in slender, white needles, m. p. 221°.

4 : 5 : 5 : 7 : 7-*Pentachloro-6-keto-2-phenyltetrahydro-2 : 1 : 3-benztriazole*, $NPh\langle\begin{matrix}N\cdot C-CCl_2-CO\\ N\cdot C\cdot CHCl\cdot CCl_2\end{matrix}$, is formed together with small quantities of the corresponding *hexachloroketochloride* by the action of chlorine on the stannichloride of either of the amino-compounds just described; it forms stout, yellowish-green, monoclinic crystals, m. p. 128°, and when reduced yields a mixture of the corresponding *dichlorohydroxy-* and *trichlorohydroxy*-compounds, which could not be resolved. 4 : 5 : 7 : 7-*Tetrachloro-6-keto-2-phenyl-6 : 7-dihydro-2 : 1 : 3-benztriazole*, $C_{12}H_5ON_4Cl_4$, prepared by boiling the pentachloro-compound just described with a solution of potassium acetate in acetic acid, crystallises in slender, yellow needles, m. p. 168°, and when reduced with stannous chloride yields 4 : 5 : 7-*trichloro-6-hydroxy-2-phenyl-2 : 1 : 3-benztetrazole*,

$$C_{12}H_6ON_3Cl_3,$$

slender, white needles, m. p. 167—168°, the *acetyl* derivative of which, $C_{14}H_8O_2N_3Cl_3$, crystallises in glistening, white needles, m. p. 179—180°. The trichlorophenol is oxidised by nitric acid (D 1·4) in glacial acetic acid, yielding 4 : 5-*dichloro-6 : 7-diketo-2-phenyl-6 : 7-dihydro-2 : 1 : 3-benztetrazole*, $NPh\langle\begin{matrix}N\cdot C-CO-CO\\ N\cdot C\cdot CCl{:}CCl\end{matrix}$, large, red crystals, m. p. 191°. The latter substance undergoes the following changes: (1) When reduced with stannous chloride, it yields 4 : 5-*dichloro-6 : 7-dihydroxy-2-phenyl-2 : 1 : 3-benztriazole*, $C_{12}H_7O_2N_3Cl_2$, which crystallises in slender, white needles, sinters at about 130°, m. p. 154—155° (decomp.) when heated slowly, m. p. 170° (decomp.) when heated rapidly; the *diacetate*, $C_{16}H_{11}O_4N_3Cl_2$, forms glistening, slender, white needles, m. 189—190°. (2) It is converted by a hot 20% aqueous solution of sodium carbonate into 5-*chloro-6-hydroxy-4 : 7-diketo-2-phenyl-4 : 7-dihydro-2 : 1 : 3-benztriazole*, $C_{12}H_6O_3N_3Cl$, large, brownish-yellow crystals, m. p. 265—266°, which, when boiled with nitric acid (D 1·4), yields the corresponding *tetraketo*-derivative, $NPh\langle\begin{matrix}N\cdot C\cdot CO\cdot CO\\ N\cdot C\cdot CO\cdot CO\end{matrix}$, crystallising in almost colourless needles, m. p. 165—170° (decomp.). (3) When treated with aniline in glacial acetic acid it yields 5-*chloro-6-hydroxy-7-keto-4-phenylimino-2-phenyl-4 : 7-dihydro-2 : 1 : 3-benztriazole*,

$$C_{18}H_{11}O_2N_4Cl,$$

which crystallises in slender, brownish-red needles with a bronzy reflex, sinters at 228°, m. p. 234—236° (decomp.).

Pentachloroketo-2-phenyltetrahydro-2 : 1 : 3-benztriazole, when acted on by a cold 5% aqueous solution of sodium hydroxide, yields the *acid*, $NPh\langle\begin{matrix}N\cdot C\cdot CCl_2\cdot CO_2H\\ N\cdot C\cdot CCl{:}CHCl\end{matrix}$, which crystallises in slender, white needles, m. p. 62—63°; the *methyl* ester, $C_{13}H_9O_2N_3Cl_4$, forms slender, silky, white needles, m. p. 67—68°. An aqueous solution of the sodium salt of the acid when boiled yields the *acid*, $N_3Ph\langle\begin{matrix}C\cdot CO\cdot CO_2H\\ C\cdot CCl{:}CHCl\end{matrix}$, long, white needles, m. p. 177°, the *methyl* ester of which, $C_{13}H_9O_3N_3Cl_2$,

crystallises in glistening, white needles, m. p. 152—153°; the acid just described also results from the action of a 5% aqueous solution of sodium hydroxide on dichlorodiketophenyldihydro-2 : 1 : 3-benztriazole.

W. H. G.

Isomeric Thiourazoles. MAX BUSCH, J. REINHARDT, and O. LIMPACH (*Ber.*, 1909, 42, 4763—4769. Compare Marckwald and Sedlaczek, Abstr., 1896, i, 231; Busch, *ibid.*, 1902, i, 322; Busch and Opfermann, *ibid.*, 1904, i, 630).—It is shown that the triazoles obtained from α-diarylthiosemicarbazides (Marckwald, Abstr., 1899, i, 503) also exist in two isomeric forms: a labile form, for example, 1 : 4-diphenyl-5-thiourazole, $SC<\begin{matrix}NPh\cdot NH\\ NPh\cdot CO\end{matrix}$, and a stable form:

$$\begin{matrix}N{=\!=}C\text{——}\\ |\ \ O<\\ PhN\text{——}C(SH)\end{matrix}>NPh$$ (compare Marckwald).

A mixture of the two compounds is formed when finely-divided α-diphenylthiosemicarbazide is suspended in benzene and shaken for two to three hours with an excess of a toluene solution of carbonyl chloride. The two urazoles are removed by shaking with 5% sodium hydroxide solution. The labile compound is precipitated on the addition of acetic acid to the alkaline liquid, and the stable compound on the addition of hydrochloric acid to the filtrate. If the mixture is shaken for a longer time, the amount of stable compound tends to increase at the expense of its isomeride. The benzene solution contains unaltered thiosemicarbazide and phenylanilinothiobiazolone (Freund and Kuh, Abstr., 1890, 1440). The labile compound crystallises in colourless needles, melts at 139—140°, but is immediately transformed into the stable compound, m. p. 220°. Its *sodium* derivative crystallises in slender, felted needles, m. p. 60°, and reacts with methyl iodide at 100°, yielding diphenylmethylurazole (Busch and Heinrichs, Abstr., 1901, i, 617). The *silver* salt is insoluble, and with methyl iodide yields the O-*methyl* derivative, $SC<\begin{matrix}NPh\cdot N\\ NPh\cdot C\cdot OMe\end{matrix}$, m. p. 88°. When benzoylated in pyridine solution the thiourazole yields N-*benzoyldiphenylthiourazole*, $C_{21}H_{15}O_2N_3S$, as yellow needles, m. p. 146°, which are stable in the presence of alkalis.

The 5-thiol-1 : 4-diphenyl*endo*-oxydihydrotriazole, when oxidised with ferric chloride, yields a *disulphide*, $(C_{14}H_{10}ON_3S)_2$, in the form of orange-yellow needles, m. p. 231—232°. The thiol yields the 5-*benzoyl* derivative, $\begin{matrix}N:C\text{———}\\ |\ \ >O\\ PhN\cdot C(S\cdot COPh)\end{matrix}>NPh$, as colourless needles, m. p. 189°. The *sodium* derivative of the thiol has m. p. 121°, and with methyl iodide and methyl alcohol at the ordinary temperature yields methyl mercaptan and 1 : 4-diphenyl-2-methylurazole.

The following diarylthiosemicarbazides also yield pairs of isomeric thiourazoles with the m. p. indicated:

2 : 4-Diarylthiosemicarbazide.	Thiourazole.	Thio*lendo*-oxy-dihydrotriazole.
4-Phenyl-2-*m*-tolyl	125°	259°
4-Phenyl-2-*m*-bromophenyl	118—119°	257
4-Phenyl-2-*m*-chlorophenyl	108—110	259—260
4-Phenyl-2-β-naphthyl	133—134	295
4-Phenyl-2-*p*-tolyl	144	239—240
4-Phenyl-2-*p*-bromophenyl	169—170	255

J. J. S.

Organic Salts of Violuric Acid. TH. ZEREWITINOFF (*Ber.*, 1909, **42**, 4802—4808).—Violuric acid forms intensely coloured salts with primary, secondary, and tertiary aliphatic amines and diamines, also with pyridine, piperidine, alkaloids, and some aromatic amines. The salts with primary aliphatic amines exist in two main forms, coloured blue and red (compare Hantzsch, Abstr., 1909, i, 331), but usually mixtures of these are obtained resulting in violet or blue, or reddish-violet salts. Usually only one form is stable, the conversion of one into the other readily taking place in the presence of moisture. Thus *n*-propylamine, *n*-butylamine, and *n*-amylamine violurates are obtained as violet salts from alcoholic solution, but become blue on exposure to moist air, and remain blue when dried in a desiccator.

Salts of violuric acid with normal primary amines are usually red or violet in colour; those derived from primary *iso*-compounds are more often blue. The blue modification is the one generally obtained from aqueous solution.

The amine violurates are prepared by mixing the components in equimolecular proportions in alcoholic solution. The salt readily separates, and may be crystallised from alcohol or water.

Methylamine violurate is obtained violet from alcoholic solution, or blue when methyl ethyl ketone is the solvent, the violet being the stable form. *Ethylamine violurate* is at first obtained blue, but rapidly passes into the stable red form. n-*Propylamine violurate* is at first obtained blue in alcoholic solution, but the salt turns reddish-violet when left in contact with the solvent. The violet form retains its colour when dried, but changes to blue again in presence of moisture. iso*Propylamine violurate* is blue; n-*butylamine violurate* is violet, changing to blue on exposure. iso*Butylamine violurate* forms violet-blue plates or blue needles. n-*Amylamine violurate* is likewise violet, changing to blue. iso*Amylamine violurate* is at first blue, but becomes violet on recrystallisation. tert.-*Amylamine violurate* is also blue; similarly, iso*hexylamine violurate*, but this is violet when crystallised from water. *Heptylamine violurate* is similar.

Diamine salts having the formula

$$R\cdot NH_3\cdot O\cdot C{<}{\begin{matrix}N{-\!-}CO\\NH\cdot CO\end{matrix}}{>}C{:}N\cdot O\cdot NH_3\cdot R$$

are prepared by keeping the monoamine violurate in presence of the corresponding amine in a desiccator.

Diisobutylamine violurate and *di*-n-*amylamine violurate* are both reddish-violet in colour.

The amine violurates dissolve in pyridine with a blue coloration. The active hydrogen atoms were determined at normal temperature

and at 85° by means of magnesium methyl iodide by the method previously described (Abstr., 1908, i, 598). The results indicate that at normal temperature only two hydrogen atoms of the NH_3 radicle are active, but at 85° all three react. E. F. A.

Hæmopyrrole. II. Z. Leyko and Leon Marchlewski (*Biochem. Zeitsch.*, 1909, **22**, 464—470; *Bull. Acad. Sci. Cracow*, 1909, 583—588. Compare Abstr., 1908, i, 710).—Altogether four products have been obtained by the action of benzenediazonium salts on hæmopyrrole. The main product has the formula

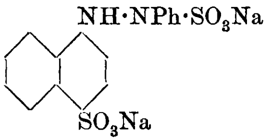
$$C_8H_{11}N(N_2Ph)_2,HCl.$$

The authors now describe a method for preparing the second product, $N_2Ph\cdot C_8H_{11}N\cdot C_8H_{11}N\cdot N_2Ph,HCl$, which melts at 268°. It can be separated from the chief product by means of chloroform, in which it is much more soluble, forming a bluish-violet solution, from which it can be precipitated by alcohol.

By means of sodium acetate the free base of this dye can be obtained. The authors give the measurements of the absorption bands of the chlorine-containing substance in chloroform solution. The results obtained are regarded as of importance as showing that hæmopyrrole corresponds with the formula $C_8H_{13}N$, and not $C_7H_{11}N$, and also that it is admixed with a second product corresponding with the formula $C_8H_{12}N\cdot C_8H_{12}N$, the representative of a new class of pyrrole derivatives. S. B. S.

Action of Sulphites on Aromatic Amino- and Hydroxyl Compounds. VIII. Behaviour of Hydrazines, especially of Phenylhydrazine, in the Sulphite Reaction. Hans Th. Bucherer and Ernst F. Sonnenburg (*J. pr. Chem.*, 1910, [ii], **81**, 1—48. Compare Abstr., 1909, i, 787).—A difference has been observed in the behaviour of naphthalene derivatives of the α- and the β-series containing only one auxochromic group when these compounds undergo prolonged boiling with phenylhydrazine and 36% sodium hydrogen sulphite. The reactions are complicated by the interaction of the two last-mentioned substances to form sodium phenylhydrazinesulphonate, from which the desired reaction product cannot be separated. After decomposing the latter, however, by alkalis and by acids, the nature of the secondary products throws some light on the constitution of the primary products in the sulphite reaction. Thus amines and naphthols of the α-series (except α-naphthol itself and 1-naphthylamine-5-sulphonic acid) yield *s*-hydrazinesulphonates, $NHR\cdot NPh\cdot SO_3Na$ or $NHPh\cdot NR\cdot SO_3Na$, which are converted by alkali into benzeneazonaphthalene derivatives, and by acid into nuclear sulphonic acids of the carbazoles, and also to some extent into diamino-compounds by the benzidine transformation. Amines and naphthols of the β-series and also the two above-mentioned exceptions of the α-series yield, after treatment with phenylhydrazine and sodium hydrogen sulphite, carbazole-*N*-sulphonic acids, which are probably produced from an initially-formed hydrazo-compound by intramolecular indole condensation; the absence of any hydrazo-compound among the primary products of the reaction is proved by the non-production of azo-compounds by treatment with alkali (compare Abstr., 1908, i, 455).

The reaction typical of members of the α-series is best exemplified by 1-naphthol-4-sulphonic acid, the only instance in which the initial hydrazo-compound can be separated from the sodium phenylhydrazinesulphonate formed simultaneously. 1-Naphthol-4-sulphonic acid is boiled with phenylhydrazine and 36% sodium hydrogen sulphite for seven and a-half hours, and the white, crystalline product is extracted with boiling 95% alcohol. The alcoholic extract deposits on cooling colourless crystals, which are freed from sodium phenylhydrazinesulphonate by treatment with benzene and with alcohol; the purified product has the composition



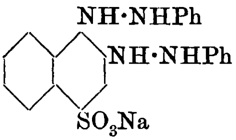
$C_{16}H_{12}O_6N_2S_2Na_2$, and is the *hydrazo*-compound, probably having the annexed constitution. By treatment with sodium hydroxide, it yields benzeneazo-α-naphthalene and benzeneazo-α-naphthalenesulphonic acid (each of which can be reduced to diamino-compounds), and by heating with hydrochloric acid (3 : 1) it is converted into α-phenonaphthacarbazole and a diamino-compound. 1-Naphthylamine-4-sulphonic acid behaves in the same way, and yields the same products, and so also does 1-naphthylamine-6-sulphonic acid, the reaction product being converted by dilute sodium hydroxide on the water-bath into benzeneazo-α-naphthalene-6-sulphonic acid, and by strong hydrochloric acid into *α-phenonaphthacarbazole-6-sulphonic acid*, $SO_3H\cdot C_{10}H_5{<}\genfrac{}{}{0pt}{}{NH}{C_6H_4}$, and a diamino-compound.

By prolonged heating with phenylhydrazine and 36% sodium hydrogen sulphite, α-naphthol yields pheno-α-naphthazole-*N*-sulphonic acid, which cannot be isolated in a solid state, but yields phenonaphthacarbazole when heated with concentrated hydrochloric acid. In a similar way, the product from 1-naphthylamine-5-sulphonic acid yields α-phenonaphthacarbazole-5-sulphonic acid (probably obtained from the *N*/5-disulphonic acid); that from 2-naphthol-1-sulphonic acid or 2 naphthylamine-1-sulphonic acid yields 2 : 1-phenonaphthacarbazole in small amount and 2 : 3-phenonaphthacarbazole-1-sulphonic acid; that from 2-naphthol-6-sulphonic acid yields phenonaphthacarbazole-6-sulphonic acid, and that from 2-naphthol-3 : 6-disulphonic acid yields a carbazole-3 : 6-disulphonic acid.

The action of phenylhydrazine and sodium hydrogen sulphite on naphthalene derivatives containing two auxochromic groups is somewhat different from that on derivatives containing only one. Carbazoles are not formed. Thus 1-amino-2-naphthol-4-sulphonic acid yields a yellow *solid* and a yellow solution. The solid has the composition $C_{22}H_{19}O_3N_4SNa$, and by treatment with hot sodium hydroxide yields a bluish-red *dye*, from which hydrochloric acid eliminates phenylhydrazine. The yellow solution by treatment with warm concentrated sodium hydroxide yields sodium 1-benzeneazo-2-naphthol-4-sulphonate, 2-benzeneazo-1-naphthol-4-sulphonate, and 2-benzeneazo-1-naphthol. Bearing in mind that the sulphite reaction proceeds thus:

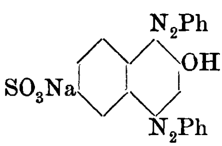
$$R\cdot NH_2 \text{ or } R\cdot OH \xrightarrow{NaHSO_3} R\cdot O\cdot SO_2Na \xrightarrow{PhN_2H_3} R\cdot NH\cdot NHPh,$$

there appears to be little doubt that the yellow solid has the annexed



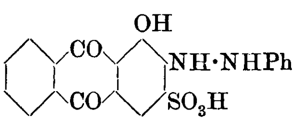
constitution, and that it yields the preceding azo-compounds by loss of phenylhydrazine from position 1 or 2 and simultaneous oxidation when treated with alkali. Similarly, 1-amino-2-naphthol-3 : 6-disulphonic acid also yields two yellow products, the one soluble, the other insoluble, which are converted by alkali into red azo dyes.

The action of phenylhydrazine and sodium hydrogen sulphite on certain azo-dyes follows a similar course. By heating 1-benzeneazo-2-naphthol-3 : 6-disulphonic acid with phenylhydrazine (or hydrazine hydrate) and sodium hydrogen sulphite, a yellow solid and a yellow solution are obtained, from each of which the original dye is recovered by alkali. The reaction in the case of 1-benzeneazo-2-naphthol-6-sulphonic acid is more profound. Again, a yellow *solid* and a yellow solution are obtained. The latter regenerates the original dye by treatment with alkali, and probably contains the hydrogen sulphite compound of the dye. The yellow solid, the analysis of which accords with the constitution $SO_3Na\cdot C_{10}H_4(NH\cdot NHPh)_2(NH\cdot NPh\cdot SO_3Na)$, is stable towards cold alkali, but is converted by warm dilute sodium hydroxide into a bluish-red *dye*, the analysis of which points to the annexed constitution.



The behaviour of a mixture of 1-benzeneazo- and 1-tolueneazo-2-naphthol-6-sulphonic acid, or of 1-xyleneazo-2-naphthol-3 · 6-disulphonic acid, with phenylhydrazine and sodium hydrogen sulphite is very similar to the preceding.

The behaviour of alizarin-red-*S* with phenylhydrazine and sodium hydrogen sulphite has also been examined. The product is a yellowish-brown *substance*, which resembles the original dye in several respects



but differs from it in the colour of its alkaline solution and in producing a more violet shade on chromed wool. It has probably the annexed constitution, and regenerates alizarin-red-*S* and phenylhydrazine when heated with dilute hydrochloric acid.

No condensation takes place when 1-naphthylamine- or 1-naphthol-4-sulphonic acid is heated with sodium hydrogen sulphite and hydrazobenzene, either together or successively; the product contains azobenzene, benzidine, and its *N*-sulphonic acid. The latter is obtained almost quantitatively when azobenzene, ammonium hydrogen sulphite, and ammonium hydroxide (D 0·88) are heated for twenty-four hours at 100—110° under 2 atmospheres pressure. C. S.

Compounds of Copper with Egg-Albumin. ALBERTO SCALA and GIUSEPPE BONAMARTINI (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 551—559).—Further examination of the acid copper albumin obtained from copper sulphate and egg-albumin (compare Bonamartini and Lombardi, Abstr., 1909, i, 72) shows that, after washing, this compound does not contain copper and sulphuric acid in the proportions in which they exist in copper sulphate, the copper always being

in excess. In fact, making allowance for the sulphuric acid yielded on analysis by the sulphur of the albumin, it would appear that the whole of the sulphuric acid is eliminated by washing, together with the larger part of the copper.

These observations may be explained by assuming that the copper sulphate combines with lateral amino-groups of the albumin molecule (compare Traube-Mengarini and Scala, Abstr., 1909, ii, 603) thus:

$$\left\langle\begin{array}{l}NH_2\\NH_2\\NH_2\\NH_2\end{array}\right. + \begin{array}{c}SO_4\\ \\Cu\end{array} \longrightarrow \left\langle\begin{array}{l}\left.\begin{array}{l}NH_3\\NH_3\end{array}\right\rangle SO_4\\ \left.\begin{array}{l}NH\\NH\end{array}\right\rangle Cu\end{array}\right. ,$$

giving a compound in which the degrees of dissociation and hydrolysis of the group ${NH_3 \atop NH_3}\!\!>SO_4$ are greater than those of the group ${NH \atop NH}\!\!>Cu$, so that whilst the one group tends to become completely removed, the other (Cu) tends towards a limit. If, then, compounds containing at first different proportions of copper are washed, they should yield compounds of constant type, and this is found approximately to be the case.

That this explanation is the true one is shown by the observation that, when an egg-albumin solution is treated with copper sulphate in slight excess and then with sodium hydroxide solution, a compound is obtained with a proportion of copper greater than is ever observed when no sodium hydroxide is employed; the alkali tends to detach the SO_4 groups, and at the same time introduce more Cu groups into the molecule. T. H. P.

The Scission Products of the Nucleo-protein of Milk Glands. JOHN A. MANDEL (*Biochem. Zeitsch.*, 1909, **23**, 245—249).—The amino-acids and hexone bases obtained by the hydrolysis of the nucleo-protein were estimated and compared with the hydrolysis products of caseinogen. There is a decided similarity in the numbers obtained, which indicate that caseinogen is possibly a degradation product of the nucleo-protein of milk glands, and produced from the latter by a scission of carbohydrates, purine, and pyrimidine bases. Hammarsten's method was employed in the preparation of the nucleo-protein. S. B. S.

Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes. SÖREN P. L. SÖRENSEN (*Biochem. Zeitsch.*, 1909, **22**, 352—356; *Compt. rend. Lab. Carlsberg*, 1909, **8**, 1—168. Compare Abstr., 1909, i, 861).—It was found that the secondary sodium phosphate employed for preparing the 1/15 mol. standard solution contained 3—4% of the primary salt. New determinations with a pure salt were accordingly made, and the results are given in a table. The new values, p_H, do not, however, differ essentially from the ones previously given except in the mixtures having the greatest alkalinity. In neutral or nearly neutral mixtures, the difference is quite small, and is sometimes positive and sometimes negative, so that the old values are retained for the whole curve. N. H. J. M.

[The Enzymes of Gum-acacia and certain other Gums.] VIKTOR GRAFE (*Zeitsch. physiol. Chem.*, 1909, **63**, 106—108).—A reply to some criticisms of Reinitzer (Abstr., 1909, i, 751). S. B. S.

Preparation of Hydroxyarylarsenious Oxides. FARBWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 213594).—The action of mild reducing agents, such as hydrogen iodide, sulphurous acid, phenylhydrazine, phosphorus trichloride, or thionyl chloride on hydroxyphenylarsinic acids leads to the formation of hydroxyarsenious oxides.

p-*Hydroxyphenylarsenious oxide*, $OH \cdot C_6H_4 \cdot AsO$, a colourless, crystalline powder, readily soluble in water or alcohol, is prepared by reducing sodium *p*-hydroxyphenylarsinate with potassium iodide and dilute sulphuric acid.

p-*Arsenophenol*, $OH \cdot C_6H_4 \cdot As\!:\!As \cdot C_6H_4 \cdot OH$, is precipitated in yellow flakes when the foregoing compound is warmed in neutral solution with sodium hypochlorite. F. M. G. M.

o-Aminoarylarsinic Acids. LUDWIG BENDA (*Ber.*, 1909, **42**, 3619—3622. Compare Ehrlich and Bertheim, Abstr., 1907, i, 812; O. and R. Adler, 1908, i, 492; Benda and Kahn, 1908, i, 591; Bertheim, 1908, i, 590).—Arylamines with a substituent in the para-position with respect to the amino-group condense with arsenic acid, yielding *o*-aminoarylarsinic acids, but the yields are not good. These ortho-arsanilic acids closely resemble the corresponding para-compounds in most of their properties, and can be readily acylated and diazotised. 4-*Aminotolyl*-5-*arsinic acid*, $NH_2 \cdot C_6H_3Me \cdot AsO(OH)_2$, obtained from *p*-toluidine and arsenic acid at 195—200°, crystallises from dilute alcohol in felted needles, m. p. 176°. *m*-Xylidine and arsenic acid yield 4-*amino*-m-*xylene*-5-*arsinic acid*, $NH_2 \cdot C_6H_2Me_2 \cdot AsO(OH)_2$, m. p. 199—200°, and *p*-chloroaniline and arsenic acid, 4-*chloro*-1 : 2-*arsanilic acid*. $NH_2 \cdot C_6H_3Cl \cdot AsO(OH)_2$, m. p. 207°. The position of the arsinic acid radicle can be determined by replacement by iodine. J. J. S.

Preparation of Carbamide and of Thiocarbamide Derivatives of *p*-Aminophenylarsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 213155).—The action of cyanic or thiocyanic acids (or the corresponding esters) on *p*-aminophenylarsinic acid or its derivatives yields crystalline compounds having the general formula $NRR_1 \cdot CR_2 \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2$, where R and R_1 may be either hydrogen, aryl, or alkyl groups, and R_2 either sulphur or oxygen; these compounds are sparingly soluble in cold water or dilute mineral acids, and therapeutically less toxic than the acyl *p*-aminophenylarsinic acids. The following examples are mentioned: *carbamidoarsanilic acid, thiocarbamidoarsanilic acid, phenylcarbamidoarsanilic acid, methylcarbamidoarsanilic acid, carbamido*-o-*methylarsanilic acid*, and *carbamidoanthranilic-arsinic acid.* F. M. G. M.

Organic Chemistry.

Oxidation of Unsaturated Compounds by means of Organic Peroxides. EDUARD LIPPMANN (*Ber.*, 1910, **43**, 464. Compare Prileschaéeff, this vol., i, 86).—The addition of benzoyl peroxide to amylene, and the subsequent hydrolysis to *iso*diamylene oxide, was studied by the author in 1884 (Abstr., 1885, 366).

J. J. S.

Condensation of *sec.*-Butyl Alcohol with its Sodium Derivative. MARCEL GUERBET (*Compt. rend.*, 1910, **150**, 183—185. Compare Abstr., 1902, i, 130, 583, 657; 1908, i, 162, 635).—When *sec.*-butyl alcohol is heated with its sodium derivative at 200—220° there is formed a mixture of two alcohols: (1) *γ-Methylheptan-ε-ol*, CHMeEt·CH_2·CHEt·OH, a liquid with a mint-like odour, has b. p. 167—169° (corr.), D^0 0·8493; its *acetate* has b. p. 183—185° (corr.). On oxidation, the alcohol yields *γ-methylheptan-ε-one*, $C_8H_{16}O$, b. p. 161° (corr.); the *semicarbazone* crystallises in needles, m. p. 96°. The constitution of the foregoing alcohol and ketone was deduced from a study of their oxidation products.

(2) The dodecyl alcohol, "*trisec.-butylic alcohol*," $C_{12}H_{26}O$, b. p. 250—255° (corr.), an agreeably smelling liquid, is converted on oxidation into the corresponding *ketone*, $C_{12}H_{24}O$, b. p. 247—248° (corr.). This forms a *semicarbazone*, m. p. 161—162°. W. O. W.

Methylacetenylcarbinol [Butinene-γ-ol]. ROBERT LESPIEAU (*Compt. rend.*, 1910, **150**, 113—114. Compare Abstr., 1908, i, 496). —A description of a method for preparing alcohols of the type OH·CHR·C⫶CH. *β-Bromo-Δ^α-butene-γ-ol*, OH·CHMe·CBr:CH_2, obtained by the action of magnesium methyl iodide on bromoacraldehyde, is a colourless liquid, b. p. 59·5—60°/14 mm., or 151°/732 mm. (decomp.); it forms a *phenylurethane*, m. p. 62·5—63·5°. Alcoholic potassium hydroxide converts the alcohol almost quantitatively into acetylene, whilst the aqueous alkali brings about a more complex change. Amongst the products recognised were acetylene, propionic acid, and *butinene-γ-ol*, OH·CHMe·C⫶CH. This was isolated, not quite free from water, as a liquid, b. p. 107—109°/760 mm. By treating with an ammoniacal cuprous chloride solution, a precipitate is formed, which, on treatment with iodine and potassium iodide, is converted into *ααβ-tri-iodo-Δ^α-butene-γ-ol*, OH·CHMe·CI:CI_2, m. p. 96°.

W. O. W.

Unsaponifiable Constituents of Japan Tallow. HERMANN MATTHES and W. HEINTZ (*Arch. Pharm.*, 1909, **247**, 650—657).— Japan tallow, m. p. 53—53·5, D 1·0032, is saponified by alcoholic potassium hydroxide, and the clear soap solution is diluted with water and extracted with ether. The residue obtained by the distillation of

the ethereal extract is submitted to a repetition of these operations. The final residue thus obtained in 0·68% yield is a yellowish-brown mass (iodine number 36·25), which is separated by petroleum into an insoluble portion, from which myricyl alcohol is isolated, and a soluble portion, from which phytosterol, m. p. 139°, and ceryl alcohol, m. p. 79°, are obtained, together with a saturated *alcohol*, m. p. 65° (*acetate*, m. p. 41°), which is probably nonadecyl alcohol, $C_{19}H_{40}O$.

C. S.

Dimethyldiethyldicarbinol [γδ - Dimethylhexane - γδ - diol]. Mlle. Cécile Frumina (*Bull. Acad. roy. Belg.*, 1909, 1151—1157).—Lawrinowitsch's pinacone, obtained by reducing methyl ethyl ketone with sodium (Abstr., 1877, ii, 427), has been prepared by the action of magnesium ethyl iodide on methyl oxalate, and proved to consist of a single liquid substance, γδ-dimethylhexane-γδ-diol,

OH·CMeEt·CMeEt·OH,

b. p. 195°/760 mm. or 10°/110 mm. The solid modification obtained by Zelinsky and Krapiwin (Abstr., 1893, i, 390) in repeating Lawrinowitsch's experiment was not produced in the synthesis now described. The *diethyl ether* has b. p. 142—143°/760 mm. or 110—111°/20 mm., and is liquid. The *dichloride* boils at 165—166°/760 mm. or at 114—115°/18 mm.

T. A. H.

Drying of Moist Ether. E. von Siebenrock (*Monatsh.*, 1909, 30, 759—766).—A comparative study of calcium chloride, potassium carbonate, sodium sulphate, magnesium sulphate, sylvite, potassium chloride, calcium sulphate, and carnallite, having regard to their use, in the anhydrous state, for the removal of water from moist ether. The first two substances mentioned are shown to be most efficacious; sodium sulphate, a substance frequently recommended and used for drying ether, is not very effective, and may be replaced with great advantage by carnallite and magnesium sulphate.

W. H. G.

Action of Sulphur and Ammonia on Organic Sulphides and Disulphides. Bror Holmberg. (*Ber.*, 1910, 43, 220—226. Compare Abstr., 1908, i, 308).—Organic sulphides and disulphides form reddish-brown additive products of the general formula R_2S_x,yNH_3 with sulphur and ammonia. The reaction is reversible, the equilibrium depending on the sulphide used. In some cases, as with ethyl and *p*-tolyl disulphides, the additive product undergoes further change into the tetrasulphide, according to the equation:

$$R_2S_x,yNH_3 \rightleftharpoons R_2S_4 + S_{x-4} + yNH_3,$$

so that the ammonia can be considered to act catalytically on the formation of tetrasulphides from disulphides and sulphur.

The organic sulphide or disulphide is dissolved in absolute alcohol, an excess of flowers of sulphur added, and the solution then saturated with ammonia, whereby the colour gradually changes to a dark brown. After some weeks the undissolved sulphur is collected and weighed, the filtrate allowed to evaporate spontaneously, and the residue then investigated.

With ethyl sulphide, the residue consisted of a minute trace of sulphur, but the additive product must have been formed in solution,

since the presence of ethyl sulphide is necessary for the formation of the brown colour.

Ethyl disulphide gave a residue of a yellow uncrystallisable oil; when this was distilled under diminished pressure (12 mm.), a colourless liquid distilled over at 77—78°, and the residue in the flask consisted of ethyl tetrasulphide.

p-Tolyl disulphide (prepared from *p*-tolyl mercaptan and sulphuryl chloride in ethereal solution, or by the spontaneous oxidation of an alkaline solution of the mercaptan) gave a solid residue, contaminated with oil, which after recrystallisation from alcohol is found to be a mixture of the di- and tetra-sulphide, the latter having m. p. 75°.

Diethyl dithiodiglycollate gave a dark-coloured solution, from which the original substances were always regenerated, no matter what the treatment; large quantities of sulphur dissolved. If the filtrate, after collecting the excess of sulphur, was again saturated with ammonia and kept for six weeks, the amide, m. p. 156—157°, derived from the original ester was formed.

In an appendix on the inorganic polysulphides, the author states his opinion that compounds with simple sulphur chains are colourless, or only pale yellow; a brown colour is due to the presence of larger atomic complexes, S_x. Whether the compound should be formulated as M_2S,S_x or M_2S_2,S_x is left undecided. T. S. P.

Crystalline Form and Optical Characters of Lead Formate. B. KARANDÉEFF (*Centr. Min.*, 1910, 17—24).—Crystals of lead formate, $Pb(CHO_2)_2$, are orthorhombic, with $a : b : c = 0·74538 : 1 : 0·84656$. Detailed determinations of the optical constants are given. L. J. S.

[Electrolysis of Carboxy-acids.] FELIX KAUFLER (*Ber.*, 1910, **43**, 266).—The statement made by the author and C. Herzog (Abstr., 1909, i, 870) in connexion with the attitude of Forster and Piguet (Abstr., 1904, i, 965) towards the superoxide theory was incorrect. An error was also made in the reference to the work of Miller and Hofer. R. V. S.

Formation of Dichloroacetic Acid from Trichloroacetaldehyde by Wallach's Method. ARTHUR KÖTZ (*Festschrift Otto Wallach*, 1909, 496—501. Compare Wallach, Abstr., 1878, 285, 288).—The conversion of chloral into dichloroacetic acid, which may be brought about through the agency of water alone, is greatly facilitated by the presence of potassium cyanide, probably owing to the intermediate formation of chloralcyanohydrin, $CCl_3·CH(OH)·CN$, and $\alpha\alpha$-dichloro-β-cyano-β-hydroxyethylene, $CCl_2:C(OH)·CN$, or the tautomeride, dichloropyruvonitrile, $CHCl_2·CO·CN$. The following observations are quoted in support of this explanation: (1) Dichloroacetic acid is formed by the action of water on chloralcyanohydrin. (2) Nitriles of dihalogenated pyruvic acids under the conditions of Wallach's method yield dihalogenated acetic acids and hydrogen cyanide. (3) Trichlorolactic acid may be converted in aqueous solution into dichloroacetaldehyde, hydrogen chloride, and carbon dioxide;

this reaction undoubtedly takes place through the intermediate formation of $\alpha\alpha$-dichloro-β-hydroxyethylenecarboxylic acid or the tautomeric dichloropyruvic acid, since dihalogenated pyruvic acids decompose in aqueous solution, yielding dihalogenated aldehydes and carbon dioxide.

Chloroacetaldehyde and dichloroacetaldehyde behave similarly to chloral, with the difference that the first-named substance cannot be converted into formic acid and chloromethane.

β-Halogenated aldehydes, such as β-chloropropaldehyde, cannot be converted into the corresponding acids even under the influence of hydrogen cyanide; it would appear, therefore, that reactions of the nature under discussion only take place when halogen and oxygen are united to adjacent carbon atoms. W. H. G.

Catalytic Phenomena. JACOB BOESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 417—421).—By the researches of Perrier (Abstr., 1900, i, 331) and the author (Abstr., 1900, i, 349; 1901, i, 474) it has been shown that in Friedel and Crafts' reaction it is not the aromatic hydrocarbon, but the chloride or anhydride, which is first attacked by the aluminium chloride, as in many cases additive products can be isolated. The author regards this initial action as consisting of a loosening of the chloride, and possibly also of the double linkings of the benzene derivative, it being known that many reactions indicate the action of aluminium chloride to be purely a dissociating one. In order to test this view, the author has examined several additional cases, and with the idea that the reaction might proceed more readily if stable chlorine compounds, such as hydrogen chloride, could be formed during the decomposition, the substances chosen were trimethylacetyl chloride, dichloroacetyl chloride, chloral and trichloroacetyl chloride; these all contain a more or less overloaded carbonyl group, so that the reaction could be followed by the evolution of carbon monoxide. The results obtained are as follows: Trimethylacetyl chloride is resolved at 0° according to the equation $CMe_3\cdot COCl = HCl + CO + C_4H_8$, the *iso*butylene being almost entirely polymerised. When gently heated, chloral undergoes decomposition in two directions: (*a*) $CCl_3\cdot CHO = HCl + CO + CCl_2$ (or C_2Cl_4), to the extent of 70—75%; and (*b*) $CCl_3\cdot CHO = CO + CHCl_3$. With dichloroacetyl chloride decomposition takes place in the two directions: $CHCl_2\cdot COCl = CO + CHCl_3$, to 60%, and $CHCl_2\cdot COCl = CO + HCl + CCl_2$, the CCl_2 presumably being polymerised to C_5Cl_{10}. Trichloroacetyl chloride, when repeatedly distilled with aluminium chloride, is decomposed in one direction: $CCl_3\cdot COCl = CCl_4 + CO$.

It is remarkable that, in spite of its excess of chlorine atoms, trichloroacetyl chloride is the most difficult of attack. The reaction seems to proceed particularly smoothly in the case where hydrogen and chlorine atoms are united with two adjacent carbon atoms.

The course of the reaction with chloral and dichloroacetyl chloride indicates that it is the movable chlorine atom which is initially rendered active. The action of aluminium chloride on trimethylacetyl chloride is too violent to admit of the first stage of the reaction being ascertained. But with sulphuric acid, which in many cases

behaves analogously to aluminium chloride and forms the same kind of additive products, the reaction appears to pass through the phases: $CMe_3\cdot COCl + H_2SO_4 = CMe_3\cdot CO\cdot SO_4H + HCl$ and $CMe_3\cdot CO\cdot SO_4H = H_2SO_4 + CO + C_4H_8$, the chlorine atom being first detached by the sulphuric acid. T. H. P.

Detergent Action of Soap Solutions. III. WALTHÈRE SPRING (*Bull. Acad. roy. Belg.*, 1909, 1059—1065; *Arch. Sci. phys. nat.*, 1910, [iv], **29**, 42—48, and *Bull. Soc. chim. Belg.*, 1910, **24**, 17—54.* Compare Abstr., 1909, i, 628, and this vol., i, 6).—The results obtained with "red ochre" (*loc. cit.*) have led to the extension of this investigation to the action of hydrated alumina on soap solutions. The results are analogous to those obtained with red ochre.

To each member of a series of fourteen solutions containing quantities of soap ranging from 1/2·5% to 1/16%, 2 c.c. of a mixture of water and aluminium hydroxide (equivalent to 0·0061% Al_2O_3) were added. The mixtures containing 1/8% and 1/16% of soap flocculated in twenty-four hours, and that containing 1/4% of soap flocculated in thirty-nine hours; the remaining mixtures, except that containing 1/2·5% soap, having in this time flocculated partially. Changes in the relative proportions of aluminium hydroxide and soap displace these points of flocculation, and also mask the periodicity. The coagulated product is pulverulent, like that obtained with ferric hydroxide (*loc. cit.*), and on ignition gives a mixture of about 3 mols. of alumina to 1 mol. of sodium carbonate, indicating an original adsorption product of 3 mols. of alumina with 2 of soap. T. A. H.

Detergent Action of Soap Solutions. IV. WALTHÈRE SPRING (*Bull. Acad. roy. Belg.*, 1909, 1128—1139, and *Bull. Soc. chim. Belg.*, 1910, **24**, 17—54 *).—Silicic acid, clay, and cellulose react with soap solutions in the same way as lampblack (Abstr., 1909, i, 628), red ochre (this vol., i, 6) and alumina (preceding abstract) forming with a part of the soap insoluble adsorption compounds, which are less adhesive than the original colloidal substances.

A soap solution in which silicic acid has been suspended, and which has been clarified by deposition, does not redden with phenolphthalein solution, and yields less alkaline ash on evaporation and ignition than the original solution, due to combination of the silicic acid with a basic portion of the soap. Such a suspension on filtration yields a filtrate containing silica, and the amount of the latter in the filtrate augments with the diminution in concentration of the soap solution (compare *loc. cit.*). Solutions of soap of strengths varying from 1/512% to 2% show periodicity in suspending power for silicic acid, the maxima being at about 1/16% and 1/2%, and the minimum at about 1/8%.

Pottery clay behaves in a similar manner. Its suspension in soap solution of any strength clears with difficulty, but a maximum suspending power is shown by a soap solution of 1/8% strength. After ignition, the clay decomposes soap less readily, and deposits much more easily from suspensions, the maximum suspending power for baked clay being shown by a soap solution of 1/32% strength.

* The last reference contains the complete paper, Parts I—IV.

Cellulose has no effect on soap in solutions containing less than 1%, but for concentrations above this the soap is decomposed, a basic portion combining with the cellulose. T. A. H.

Xanthic Acid and Dixanthogen [Ethyl Di-oxythiocarbonate]. II. MANFRED RAGG (*Chem. Zeit.*, 1910, **34**, 82—84. Compare Abstr., 1908, i, 604).—A pure xanthate can only be prepared when water is excluded from the reaction mixture in order to prevent hydrolysis. To prepare sodium xanthate, sodium is dissolved in excess of ethyl alcohol, and then the calculated quantity of carbon disulphide added, the reaction mixture being stirred and cooled meanwhile. The solution so obtained is fairly stable, and gives a yellow precipitate with copper salts which is free from the dark brown impurities which are formed when hydrolytic products are present. The yellow precipitate consists of cuprous xanthate and ethyl di-oxythiocarbonate, the reaction taking place quantitatively according to the equation: $4NaS{\cdot}CS{\cdot}OEt + 2CuSO_4 = Cu_2(S{\cdot}CS{\cdot}OEt)_2 + S_2(CS{\cdot}OEt)_2 + 2Na_2SO_4$. The dixanthogen can be extracted from the precipitate by means of carbon tetrachloride. It is noteworthy that if sodium is added to a mixture of ethyl alcohol and carbon disulphide, sodium xanthate is not formed, but a compound which gives a dark red precipitate with copper salts, and only changes into yellow cuprous xanthate on warming.

The following dixanthogens [di-oxythiocarbonates] and xanthates have been prepared in a similar manner from the corresponding alcohols:

Methyl di-oxythiocarbonate, $S_2(CS{\cdot}OMe)_2$, is a brownish-yellow, viscid oil, with an odour different from that of the ethyl compound, and somewhat similar to that of acetone; D = 1·180; b. p. 122° (decomp.). *Cuprous methyl xanthate* is a pale yellow powder.

n-*Propyl di-oxythiocarbonate*, $S_2(CS{\cdot}OPr)_2$.—Brown liquid with no characteristic odour; D = 1·087; b. p. 117° (with decomposition). *Cuprous* n-*propyl xanthate* forms a pale yellow powder.

iso*Butyl di-oxythiocarbonate*, $S_2(CS{\cdot}O{\cdot}C_4H_9)_2$, is a yellow oil; D = 1·080; b. p. 165°. In the preparation of sodium *iso*butyl xanthate, it is necessary to use a large excess of the alcohol and to warm the reaction mixture. After the addition of the copper salt, the excess of *iso*butyl alcohol must be extracted with 40% ethyl alcohol, in which both the cuprous xanthate and the dioxythiocarbonate are insoluble. *Cuprous* iso*butyl xanthate* is a light yellow powder.

Amyl di-oxythiocarbonate, $S_2(CS{\cdot}O{\cdot}C_5H_{11})_2$, was prepared from ordinary commercial amyl alcohol. Dark yellow oil; D = 1·007; b. p. 158°. *Cuprous amyl xanthate* is pale yellow in colour.

Benzyl di-oxythiocarbonate, $S_2(CS{\cdot}O{\cdot}C_7H_7)_2$.—Yellow oil with a characteristic, but not unpleasant odour; D = 1·218. *Cuprous benzyl xanthate* is coloured pale yellow, and is stable up to 60°. *Sodium benzyl xanthate* can be recrystallised from alcohol, but the aqueous solution gradually decomposes.

Attempts to prepare glycerol derivatives were unsuccessful, although the results obtained point to the existence of a cuprous glyceryl monoxanthate. T. S. P.

Addition of Acid Anhydrides to Aldehydes and Ketones. RUDOLF WEGSCHEIDER and ERNST SPÄTH (*Monatsh.*, 1909, **30**, 825—869).—Acid anhydrides, for example, the anhydrides of acetic acid, propionic acid, chloroacetic acid, and benzoic acid, react with aldehydes in the presence of sulphuric acid, yielding di-esters of the aldehyde hydrates; of all the aldehydes investigated, citronellal alone did not behave in this manner, owing to the extreme readiness with which it is decomposed by acids. In the absence of sulphuric acid and at high temperatures, esters of the enolic form of the aldehyde are chiefly formed (compare Semmler, Abstr., 1909, i, 364). The mode of action of the sulphuric acid is not clear; that the mixed anhydride which is possibly formed is directly concerned in the esterification of the aldehyde is not probable, for the sulphuric acid may be replaced by hydrochloric acid, in which case the mixed anhydride is acetyl chloride, but acetyl chloride reacts with aldehydes, yielding acetates of chlorinated alcohols and only very small quantities of aldehyde diacetates. The sulphuric acid may likewise be replaced by nitric acid, phosphoric acid, or oxalic acid, but not by 3-nitrophthalic acid, although this is a stronger acid than oxalic acid; possibly the acid, in this case, is converted into the anhydride, and is thus replaced by acetic acid.

Attempts to acetylate acetone, acetophenone, and benzophenone have proved unsuccessful.

The aldehyde diacetates are hydrolysed quite readily by hot water, and are decomposed by phenylhydrazine, with the formation of aldehyde phenylhydrazones and $\alpha\beta$-acetylphenylhydrazine. The dibenzoates are hydrolysed by hot, but not by cold, aqueous potassium hydroxide.

Certain of the compounds mentioned later are extremely poisonous.

The following compounds, all of which have been prepared by various investigators in different ways, are readily obtained by the interaction of the aldehyde and acid anhydride under the influence of sulphuric acid: methylene diacetate, ethylidene diacetate, heptylidene diacetate, chloral diacetate, crotonaldehyde diacetate, cinnamylidene diacetate, ethylidene dipropionate, chloral bischloroacetate, b. p. 168°/10 mm. (compare Gabutti, Abstr., 1900, i, 370), and methylene dibenzoate. The interaction of salicylaldehyde and acetic anhydride in the presence of sulphuric acid leads to the formation of *o*-acetyloxybenzaldehyde diacetate; salicylaldehyde diacetate is not formed, as stated by Perkin (*Annalen,* 1868, **146**, 371), neither could it be obtained in the manner described by Barbier (Abstr., 1880, 468).

Propylidene diacetate, $C_7H_{12}O_4$, is a colourless liquid, b. p. 184—185° (corr.); iso*butylidene diacetate*, $C_8H_{14}O_4$, is a liquid with a not unpleasant odour, b. p. 189° (corr.); *benzylidene dipropionate*, $C_{13}H_{16}O_4$, is an oil, b. p. 158—159°/10 mm.; *chloral dibenzoate*, $C_{16}H_{11}O_4Cl_3$, forms large, well-defined, glistening crystals, m. p. 63—65°; *benzylidene dibenzoate*, $C_{21}H_{16}O_4$, crystallises in long, silky needles, m. p. 61—62°; o-*nitrobenzylidene dibenzoate*, $C_{21}H_{15}O_6N$, is dimorphous, m. p. 123—124° and 147—148°; it decomposes when distilled in a vacuum, yielding *o*-nitrobenzaldehyde and benzoic acid; m-*nitro benzylidene dibenzoate* forms rosettes of silky, white crystals, m. p.

97—99°; the *para*-isomeride has m. p. 118°; *cinnamylidene dibenzoate*, $C_{23}H_{18}O_4$, crystallises in needles, m. p. 133—135°.

Ethylidene dibenzoate, $C_{16}H_{14}O_4$, could not be prepared by the sulphuric acid method; it is obtained by the action of benzoic anhydride on ethylidene diacetate in the presence of a small quantity of sulphuric acid at 100°, and forms small, glistening crystals, m. p. 70—71°. W. H. G.

Vicianose, a New Reducing Sugar Containing C_{11}. GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1910, **150**, 180—182. Compare Abstr., 1906, i, 68; 1908, i, 817).—The cyanogenetic glucoside observed by Bruyning (Abstr., 1900, ii, 160) in the seeds of *Vicia angustifolia* undergoes hydrolysis when treated with a diastase occurring in the seeds. A new sugar, *vicianose*, $C_{11}H_{20}O_{10}$, has been isolated from the products of hydrolysis. This is the first biose isolated from a glucoside. The compound crystallises in spherular aggregates of small needles; it is very soluble in water, but only sparingly so in alcohol. A 10% aqueous solution, after fifteen minutes, shows $\alpha_D^{20-22} + 15\cdot8°$ (300 mm. tube), but after twenty-two hours the rotation remains constant at $\alpha_D^{20} + 9\cdot32° = [\alpha]_D + 39\cdot72°$. Vicianose has m. p. about 210°; it has a somewhat higher cupric reducing power than maltose, and is not fermented by yeast. W. O. W.

Theory of the Nitration of Cellulose. ALEXIS V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1712—1741. Compare Abstr., 1907, i, 390).—The author first discusses the work of previous investigators on the action of nitric acids of various concentrations, either alone or mixed with sulphuric acid, on cellulose.

The non-homogeneity of nitro-cellulose is due largely to the dilution of the nitrating mixture by the water developed in the reaction, the external parts of the mass being more highly nitrated than the inner parts. The final degree of nitration is influenced by the reversibility of the process. If the nitric acid employed is sufficiently concentrated to form nitric ethers of cellulose, and if it is in sufficiently great excess, chemical action proceeds very rapidly. Thus, with a mixture containing 23·8% HNO_3, 71·5% H_2SO_4, and 4·7% water at 20°, it was found that, after two minutes, only 1·8% of the cellulose (cotton) remained unattacked, the nitrated part containing 12·7% of nitrogen, corresponding with the introduction of $10NO_3$; after five minutes, $11NO_3$ were introduced. These results, together with those obtained with a nitrating mixture composed of 30% HNO_3, 65% H_2SO_4, and 5% H_2O, are in accord with those obtained by Lunge and Bebie (Abstr., 1901, i, 508).

Ternary mixtures of sulphuric and nitric acids and water were investigated by determining the densities, electrical conductivities, and partial pressures of the vapours of nitric acid in the mixtures (compare Abstr., 1904, ii, 251, 558, 614; 1905, ii, 583). The results obtained indicate that in such mixtures there occurs a reversible process of the type: $HNO_3,nH_2O + H_2SO_4 \rightleftarrows HNO_3,(n-x)H_2O + H_2SO_4,xH_2O$. This dehydration of nitric acid reaches a limit with a mixture of the composition corresponding with the equation:

$$HNO_3 + xH_2SO_4 + xH_2O = HNO_3 + x(H_2SO_4,H_2O),$$

further addition of sulphuric acid resulting in the formation of nitric anhydride. The results of the investigation of these ternary mixtures are given in the form of a triangular diagram (compare Abstr., 1907, i, 390).

The relation between the composition of the nitrating mixture and the degree of nitration of cellulose is discussed with the help of a large number of numerical results. T. H. P.

Synthesis of the Phospho-organic Acid of the Seeds of Plants (Posternak's Anhydroxymethylene-diphosphoric Acid). ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 23—27).—By the interaction of inosite and phosphoric acid in a current of carbon dioxide, the author has prepared an acid, $C_6H_{18}O_{24}P_6$, which exhibits all the physical and chemical characters of the phospho-organic acid obtained from the seeds of plants (compare Abstr., 1909, i, 203). By treating its barium or calcium salt with cupric and sodium acetates, the salt $C_6H_6O_{24}Cu_4Ba_2$ or $C_6H_6O_{24}Cu_4Ca_2$ is obtained, whilst the calcio-magnesium salt agrees in chemical and physical properties with the corresponding derivative of the phytin extracted from rice bran (*loc. cit.*). On hydrolysis, the acid yields compounds poorer in phosphorus, one of which, *inosite-diphosphoric acid*, $C_6H_{14}O_{12}P_2$, was isolated as a white, deliquescent, vitreous mass, and its *barium* salt, $C_6H_{10}O_{12}P_2Ba_2$, prepared and analysed. T. H. P.

Phosphoric Acid Esters of Carbohydrates. I. On Sucrose-phosphoric Acid. CARL NEUBERG and H. POLLAK (*Biochem. Zeitsch.*, 1910, **23**, 515—517).—Sucrose in water, freshly prepared calcium oxide, phosphoryl chloride, and dry chloroform were kept together at the temperature of melting ice, and the following reaction took place:

$$2C_{12}H_{22}O_{11} + 2POCl_3 + 5CaO = 3CaCl_2 + H_2O + 2C_{12}H_{12}O_{10}\cdot O\cdot PO_3Ca.$$

The sucrose-phosphate of calcium was separated out and analysed; it is a fine, white powder, readily soluble in water. The entrance of phosphoric acid into the sucrose molecule completely abolishes its fermentability. W. D. H.

Lipoproteins and the meaning of Fatty Degeneration in Cells. V. Further Syntheses of Lipopeptides. VI. Further Researches on the Cleavage of Lipopeptides. S. BONDI and FRANZ EISSLER (*Biochem. Zeitsch.*, 1910, **23**, 499—509, 510—513. Compare Abstr., 1909, i, 458, 459).—In continuation of former work, and by the use of the same methods, the following were prepared: Butyrylglycine, m. p. 70°. Butyrylalanine, thin prisms, m. p. 88—93°; its *ethyl* ester has b. p. 135—145°/14 mm. Butyrylalanylglycine, thin prisms, m. p. 171°. Palmitylalanylglycine, needles, m. p. 128—138°, not sharp. Laurylalanylglycine, groups of needles, m. p. 141°. *iso*Valerylglycine, thin prisms, m. p. 87—90. Laurylpeptone, crystalline. Palmitylpeptone, a brownish-yellow powder. Witte's peptone was used in the preparation of the two last-named substances. Unlike proteins and nearly all non-aromatic amino-acids, they are all readily soluble in alcohol. They are insoluble in light petroleum, and almost so in ether.

Butyrylglycine is not resolved by pepsin or trypsin, but is by an extract of autolysed kidney; butyrylalanine is only slightly decomposed by a similar extract of liver. Trypsin has also no action on butyrylalanylglycine or laurylalanylglycine. The latter substance, however, is decomposed by autolysed kidney extract. No evidence of reversible action was found. W. D. H.

A New Method of Forming *iso*Cyanates [Carbimides] and Hofmann's Thiocarbimide Reaction. II. RICHARD ANSCHÜTZ (*Annalen*, 1910, **371**, 201—226. Compare Abstr., 1908, i, 326).—The behaviour of the mercuric and chloromercuric salts of ethylthiolcarbamic acid and *iso*butylthiolcarbamic acid when heated alone, likewise the decomposition of mercuric and chloromercuric ethyldithiocarbamates by boiling water and by heat alone, has been investigated quantitatively, with the result that the conclusions published previously (*loc. cit.*) have to be modified slightly.

Chloromercuric ethylthiolcarbamate when heated decomposes thus: $3NHEt{\cdot}CO{\cdot}SHgCl \longrightarrow Hg_3S_2Cl_2 + COS + 2EtNCO + NH_3EtCl$; in this way it is possible to prepare alkylcarbimides without difficulty. The corresponding ethyldithiocarbamate is decomposed by heat analogously.

Mercuric ethylthiolcarbamate when heated alone decomposes into red mercuric sulphide, carbonyl sulphide, and *s*-diethylcarbamide; the formation of hydrogen sulphide could not be detected, owing to the readiness with which it interacts with ethylcarbimide, yielding carbonyl sulphide and *s*-diethylcarbamide. Mercuric ethyldithiocarbamate, when similarly treated, decomposes in two ways, represented by the equations: $[NHEt{\cdot}CS{\cdot}S]_2Hg \longrightarrow$ (1) $HgS + CS_2 + CS(NHEt)_2$ or (2) $HgS + H_2S + 2EtNCS$; the mercuric sulphide obtained in these reactions is black. The extent to which the reaction represented by (2) takes place depends on the rate of heating, for hydrogen sulphide and ethylthiocarbimide interact, yielding carbon disulphide and *s*-diethylcarbamide. The salt undergoes the same change when boiled with water, but to a greater extent (about 50%) in the manner indicated by (2). In the preparation of alkylcarbimides by Hofmann's method, however, an excess of mercuric chloride is employed; this results in the formation of chloromercuric ethyldithiocarbamate, which is decomposed by boiling water, thus: $NHEt{\cdot}CS{\cdot}SHgCl = HgS + SCNEt + HCl$.

The *iso*butyl salts undergo the same changes as the analogous ethyl compounds.

Chloromercuric ethyldithiocarbamate is prepared by adding an aqueous solution of ethylammonium ethyldithiocarbamate to a cold solution of mercuric chloride in acetone; it crystallises in white leaflets. W. H. G.

Ethyl Oxalosuccinonitrile and Diethyl Dioxalosuccinonitrile. WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1910, **43**, 228—234. Compare Abstr., 1908, i, 965).—Ethyl oxalosuccinonitrile has m. p. 112—113°, not 102—103° as previously stated. A better yield is obtained if the method of preparation formerly given is modified

so as to ensure the presence of an excess of succinonitrile throughout the reaction. According to observations made by A. Hantzsch and H. Ley, alcoholic solutions of the β-form fluoresce. H. Ley and von Engelhardt find that $0{\cdot}005N$-alcoholic solutions of the α-form also fluoresce, but the fluorescence disappears when an excess of sodium ethoxide is added, so that it is due to the presence of a small proportion of the β-form.

By doubling the quantities of ethyl oxalate and potassium ethoxide taken, and reversing the order of addition in the method formerly described for the preparation of ethyl oxalosuccinonitrile, the *dipotassium* salt of *diethyl dioxalosuccinonitrile* may be obtained (compare Michael, Abstr., 1903, i, 736). The substance gives a deep reddish-brown coloration with ferric chloride, and ammonia is evolved when it is boiled with ammonium chloride. On acidifying its aqueous solution, the *monopotassium* salt is precipitated. It forms small, lustrous needles, m. p. above 140° (decomp.), and gives a red coloration with ferric chloride. Copper acetate yields with both potassium salts and with the free nitrile the same *monocopper* salt, in the form of small green needles, which become brown at 170°, and melt at 220—225°. By acidifying an aqueous solution of the potassium salt, the *enolic* form of *diethyl dioxalosuccinonitrile* may be obtained as a viscous, brown oil, which, on shaking with water, yields a hydrate which forms colourless needles, m. p. 52—53°, gives a weak red coloration with ferric chloride, and is probably the *dihydrate*. It readily loses water, forming the *monohydrate*, m. p. 102—104°. This hydrate also gives a weak red coloration with ferric chloride. The enolic form and its hydrates change spontaneously into the ketonic form, which crystallises in yellow prisms, m. p. 123—124° (Michael, *loc. cit.*). The alcoholic solutions of this substance do not fluoresce. It is probably a ketonic enol of the constitution :

$$CO_2Et{\cdot}CO{\cdot}CH(CN){\cdot}C(CN){:}C(OH){\cdot}CO_2Et.$$

R. V. S.

Carbon Subnitride, C_4N_2. CHARLES MOUREU and J. CH. BONGRAND (*Compt. rend.*, 1910, **150**, 225—227).—This substance has been obtained by the elimination of $2H_2O$ from acetylenedicarboxylamide,

$$NH_2{\cdot}CO{\cdot}C{:}C{\cdot}CO{\cdot}NH_2;$$

it may therefore be regarded as dicyanoacetylene, $NC{\cdot}C{:}C{\cdot}CN$. The analysis of the compound presented difficulties, but it has been shown to contain less than 0·6% of hydrogen. Carbon subnitride occurs as slender, colourless needles, m. p. 20·5—21°, b. p. 76°/753 mm., D_4^{25} 0·9703. The vapour is powerfully irritant, and has an odour resembling that of cyanogen ; at 130° it is spontaneously inflammable in air, burning with a flame like that of cyanogen. The molecular refractions for the D-sodium line and for the α-, β-, and γ-hydrogen lines have been determined : M_D 21·641 ; $M_\gamma—M_\alpha$ 1·023. Refraction and dispersion are considerably higher than the values calculated on the assumption that the compound has the foregoing constitution (compare Abstr., 1906, ii, 1), probably through the contiguity of the three triple linkings.

The vapour density between 56° and 184° is in agreement with the formula C_4N_2.

W. O. W.

Naphthene Formation. IV. Formation of Naphthene from Olefines and from Artificial Lubricating Oil and the Synthesis of the Latter. CARL ENGLER and O. ROUTALA (*Ber.*, 1910, **43**, 388—397).—The conversion of olefines into naphthenes does not, as a rule, take place directly. Probably, in the first place, polymerisation to polyolefines takes place, and these, on account of their content of labile hydrogen atoms, yield, firstly, paraffins, and subsequently decompose into naphthenes, on the one hand, and lubricating oils, on the other.

When the decomposition is carried out at low temperatures, for example, with aluminium chloride at the ordinary temperature, or at the boiling point of amylene, relatively little naphthene is formed along with paraffins and lubricating oil; at higher temperatures relatively more naphthene is formed, and the lubricating oils in part decompose, forming naphthene.

When amylene is heated in tubes under pressure, methane and hydrogen are formed. By the action of aluminium chloride on amylene in the cold, an oil is formed containing more than 87% of carbon, having the composition C_nH_{2n-6}, and agreeing in composition and properties with natural lubricating oil.

When heated for some time at 350°, the lubricating oil gives rise to a mixture of unsaturated and saturated hydrocarbons; the lower boiling fractions are in the main homologues of methane, the higher boiling fractions contain increasing proportions of naphthenes.

E. F. A.

Naphthene Formation. V. The Products of Heating Cylinder Oil Under Pressure. CARL ENGLER and B. HALMAI (*Ber.*, 1910, **43**, 397—405).—Large quantities of a Baku cylinder oil were heated from four to six hours under pressure at 400—430°. The product (b. p. 25—250°) was carefully fractionated, and the constituents of the successive fractions identified. The earlier fractions contained almost entirely paraffin hydrocarbons; as the boiling point rose, the proportion of naphthenes present increased. The highest boiling fractions consisted of lubricating oils, which behaved in a similar manner to the natural oils and those synthesised from amylene.

E. F. A.

Naphthene Formation. VI. Possible Formation of Hydrocarbons in Nature, and the Origin of the Optical Activity of Petroleum. CARL ENGLER (*Ber.*, 1910, **43**, 405—411. Compare preceding abstracts).—In nature, bituminated animal and plant residues break down into solid paraffins, olefines, and liquid paraffins. The effect of heat and pressure, in conjunction with long periods of time, causes the solid paraffins to break down into liquid paraffins and olefines. The olefines condense to polyolefines; this gives rise to liquid paraffins, naphthenes, and lubricating oils; the last at a still higher temperature undergo further decomposition into liquid paraffins, naphthenes, and lubricating oils with less hydrogen. None of these changes is reversible. They take place simultaneously, and no great heat is required if the period of time be long enough. The petroleums

which have been exposed to the highest temperature contain most naphthenes and lubricating oils, although they may be younger in the geological sense than oils which contain mostly paraffins and have been exposed to lower temperatures.

The explanation given is in agreement with the fact that oils rich in naphthenes are usually rich in lubricating oils and vice versâ. The higher boiling fractions of the heated natural cylinder oil (see previous abstract) still preserve some optical activity, and it would appear that the optically active constituents of petroleum oppose great resistance to racemisation by heat. Inasmuch as the heat in the natural process is probably less than that used experimentally, the fact that the natural petroleums are optically active is not in opposition to the combined heat and pressure theory of their formation. E. F. A.

Relation between Colour and Constitution. IWAN OSTROMISSLENSKY (*Ber.*, 1910, **43**, 197—198).—A claim for priority. Werner's observations on nitro-compounds and his deductions therefrom (this vol., i, 20) had been made by the author in a paper sent to, but not published by, the German Chemical Society. C. S.

Hydrocarbons from Cinnamyl Chloride, CHPh:CH·CH$_2$Cl. HANS RUPE and J. BÜRGIN (*Ber.*, 1910, **43**, 172—178).—Cinnamyl chloride, prepared by the action of hydrogen chloride gas on cinnamyl alcohol (compare Emde, Abstr., 1909, i, 708), is a mobile liquid, b. p. 116—117°/12 mm., solidifying to large, colourless needles, m. p. 8—9°. *Cinnamyl bromide* is obtained on heating cinnamyl alcohol with phosphorus tribromide in benzene solution in colourless needles, m. p. 30°, b. p. 130°/10 mm.

Cinnamyl chloride reacts with magnesium in ethereal solution; the product when decomposed with water yields a mixture of two hydrocarbons.

αζ-Diphenyl-Δ^{αε}-hexadiene, CHPh:CH·CH$_2$·CH$_2$·CH:CHPh, forms thin, irregular, colourless, lustrous plates, m. p. 82°, b. p. 211°/11 mm., which in solution show a reddish-blue fluorescence. It yields a *tetrabromide*, separating in colourless, feathery needles, m. p. 194°.

αδ-Diphenyl-Δ^{α}-hexene, CHEtPh·CH$_2$·CH:CHPh, is a colourless, mobile fluid, b. p. 190°/11 mm., D^{20} 0·9915, n_D^{20} 1·588; the *hydrobromide* is a dark viscid oil. The constitution is indicated by the fact that, on oxidation with potassium permanganate, benzoic acid and phenylsuccinic acid are formed.

γ-Chloro-α-phenylpropane could not be prepared. *γ-Bromo-α-phenylpropane* is obtained by the action of phosphorus tribromide on hydrocinnamyl alcohol; the colourless liquid has b. p. 109°/11 mm. The bromide interacts with magnesium, forming propylbenzene and diphenylhexane. E. F. A.

Mobility of the Hydrogen Atoms of the Methylene Group in Compounds of the General Formulæ R·SO$_2$·CH$_2$·CN, R·SO$_2$·CH$_2$·CO·NH$_2$, R·SO$_2$·CH$_2$·CO$_2$Et. JULIUS TRÖGER and E. LUX (*Arch. Pharm.*, 1909, **247**, 618—649).—The

close analogy between β-sulphonecarboxylic acids and β-ketonic acids, studied by Rössing (Abstr., 1890, 781) and Engelhardt (*J. pr. Chem.*, 1889, [ii], **40**, 540) and further illustrated by Michael and Comey by the preparation of the sodium and alkyl derivatives of the former (Abstr., 1884, 319; 1885, 906; 1890, 781), suggests that the groups RSO_2 and CO_2Et exert the same influence as the groups RCO and CO_2Et on the neighbouring methylene group. The mobility of the methylene hydrogen atoms in arylsulphoneacetonitriles has already been shown to some extent by Tröger and Hillë (Abstr., 1905, i, 336), whilst the similar behaviour of such nitriles and phenylacetonitrile with amyl nitrite and sodium ethoxide and with aldehydes and sodium hydroxide has been manifested by Tröger and Prochnow (Abstr., 1908, i, 798). The present paper deals with the influence on the methylene hydrogen atoms of compounds $RSO_2\cdot CH_2X$ exerted by different groups X (where $X = CO_2R$, $CO\cdot NH_2$, or CN), the case of arylsulphonated acetamides being of special interest, since Tröger and Lindner (Abstr., 1908, i, 633) have shown that the methylene hydrogen atoms of the corresponding arylsulphonated thioacetamides are not replaceable by alkali metals or alkyl groups. The results of experiments on arylsulphonated acetonitriles, amides, and esters with alkalis, alkyl halides, aldehydes, and amyl nitrite and sodium ethoxide show that in these compounds the group $CO\cdot NH_2$ does not act like CN, and exerts an influence similar to, but weaker than, that of the group CO_2Et. For example, with alkalis, arylsulphonated acetic acids yield carbon dioxide and sulphones; their esters yield disodium derivatives; arylsulphonated acetamides are insoluble in sodium hydroxide, and arylsulphonated acetonitriles, although soluble in dilute sodium hydroxide, are not hydrolysed even by boiling, this only being effected by concentrated hydrochloric acid under pressure. The action of alkali and alkyl halides on

$$RSO_2\cdot CH_2\cdot CO_2Et$$

leads, as is known, to the formation of mono- and di-alkyl derivatives, on $RSO_2\cdot CH_2\cdot CN$ only to the production of dialkyl derivatives, and on $RSO_2\cdot CH_2\cdot CO\cdot NH_2$ results in simple hydrolysis by the alkali.

Amyl nitrite and sodium ethoxide simply hydrolyse arylsulphonated acetic esters, but react smoothly with the amides and nitriles to form *iso*nitroso-compounds by replacement of the methylene hydrogen atoms. The compounds obtained from the nitriles have the formula

$$RSO_2\cdot C(:NOH)\cdot CN,$$

and the following oximes and their derivatives are described; the *sodium* and *silver* salts are yellow powders, and the *lead* salts yellowish-white powders.

R.	m. p.	Methyl ether, m. p	Benzyl ether, m. p.	Benzoyl derivatives, m. p.	Acetyl derivatives, m. p.
Ph	—	57°	75°	153°	91°
$p\text{-}C_6H_4Me$	—	99	90	—	—
$p\text{-}C_6H_4Cl$	147°	115	80	162	126
$p\text{-}C_6H_4Br$	—	125	98	171	149
$p\text{-}C_6H_4I$	171	125	129	175	166
$OMe\cdot C_6H_4$	152	94	102	—	—
$OEt\cdot C_6H_4$	147	87	97	—	—

The following compounds, $RSO_2\cdot C(:NOH)\cdot CO\cdot NH_2$, are obtained in

a similar way, but less readily from arylsulphonated acetamides; the figures are m. p.'s: R = Ph, 153° (decomp.); R = p-C_6H_4Cl, 155° (decomp.); R = p-C_6H_4Br, 152° (decomp.); R = p-C_6H_4I, 178° (decomp.); the *sodium*, *silver*, and *lead* salts have been prepared.

Tröger and Prochnow (*loc. cit.*) have shown that arylsulphonated acetonitriles, like phenylacetonitrile, readily condense with certain aromatic aldehydes in the presence of a little sodium hydroxide. Arylsulphonated acetamides or acetic esters do not condense with aldehydes as a rule, but from salicylaldehyde the same compounds, $\begin{matrix} RSO_2\cdot C\text{——}CO \\ \Vert \qquad\qquad \\ CH\cdot C_6H_4 \end{matrix}\!\!>\!O$, are obtained by loss of water and ammonia and water and ethyl alcohol respectively. Of such compounds, the following are mentioned: R = Ph, 219°; R = p-C_6H_4Cl, 243°; R = p-C_6H_4Br, 244°; R = p-C_6H_4I, 248°.

The bromination of arylsulphonated acetic acids, esters, and amides does not proceed smoothly, but the nitriles yield compounds,

$$RSO_2\cdot CBr_2\cdot CN,$$

which are also obtained by the action of bromine on the sodium salts of the corresponding oximes: R = Ph, 123°; R = p-C_6H_4Cl, 126°; R = p-C_6H_4Br, 129°; R = p-C_6H_4I, 131°. C. S.

Aniline Antimonyl Tartrate. PAUL YVON (*Compt. rend.*, 1910, **150**, 283—285).—Clarke's salt, $C_4H_5O_6(SbO)\cdot C_6H_7N$ (Abstr., 1882, 1051), separates with 1 mol. H_2O when allowed to crystallise from an aqueous solution at 15°; the crystals deposited at 35° are anhydrous. The hydrated salt forms stellate clusters of long prisms, which become opaque on exposure, losing water of crystallisation.

In 2—5% aqueous solution, the anhydrous salt has $[\alpha]_D^{17}$ 121·28°, D^{18} 2·112; one gram of the substance is soluble in 6·36 grams of water at 15°. The hydrate has $[\alpha]_D^{19}$ 115·61°, D^{20} 1·569.

The solubilities in water and alcohol at different temperatures are given, and also crystallographic details of the anhydrous salt. W. O. W.

Complex Compounds of Aluminium Bromide with Organic Compounds. IWAN A. KABLUKOFF and AL. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1755—1762. Compare Menschutkin, Abstr., 1909, i, 897, 900).—Investigation of the melting-point curves of mixtures of aluminium bromide with benzene, toluene, xylene, naphthalene, dibromomethane, bromobenzene, and p-dibromobenzene indicates either a slight tendency of these organic compounds to give double compounds with aluminium bromide, or the extreme instability of such complex compounds. It seems, indeed, that for stable compounds to be formed with aluminium bromide, the presence of oxygen or nitrogen in the organic component is a necessary condition.

With aniline, four compounds are formed by aluminium bromide: $Al_2Br_6,2NH_2Ph$, m. p. 90°; $Al_2Br_6,3NH_2Ph$, m. p. 114°;

$$Al_2Br_6,4NH_2Ph,$$

m. p. 105°; $Al_2Br_6,8NH_2Ph$, m. p. 122°. These compounds dissolve in benzene or ether, and are decomposed by water, giving aluminium hydroxide and aniline hydrobromide.

p-Bromoaniline gives two compounds: $Al_2Br_6,2C_6H_4Br\cdot NH_2$, m. p. 140°, and $Al_2Br_6,5C_6H_4Br\cdot NH_2$, m. p. 125°. Diphenylamine gives the compound $Al_2Br_6,2NHPh_2$, m. p. somewhat above 200°; dimethylaniline, $Al_2Br_6,2NMe_2Ph$, m. p. 95°; methylaniline,

$$Al_2Br_6,2NHMePh,$$

m. p. 78°; nitrobenzene, $Al_2Br_6,2Ph\cdot NO_2$, m. p. 84°; pyridine, $Al_2Br_6,4C_5NH_5$, m. p. about 170° (decomp.); benzonitrile, the three compounds: $Al_2Br_6,2Ph\cdot CN$, m. p. 140—150°; $Al_2Br_6,3Ph\cdot CN$, m. p. about 140°, and $Al_2Br_6,4Ph\cdot CN$, m. p. about 150°.

Of the oxygenated compounds, acids, alcohols, aldehydes, and ketones form double compounds with aluminium bromide (compare Walker and Spencer, Trans., 1904, **85**, 1106). Further, esters of benzoic acid give compounds of the formula $Al_2Br_6,2Ph\cdot CO_2R$, that formed by methyl benzoate having m. p. 100°. Esters of fatty acids react energetically with aluminium bromide, hydrogen bromide being evolved.

The double compounds formed by aluminium bromide with organic nitrogen compounds are more stable than those containing organic oxygen compounds. The existence of complex compounds containing an odd number of molecules of an organic compound leads to the conclusion that the aluminium bromide present exists in the form of a doubled molecule, Al_2Br_6. T. H. P.

Preparation of Sodium Arylimides. Deutsche Gold- & Silber-Scheide-Anstalt (D.R.-P. 215339).—The replacement of an aminic hydrogen atom by sodium in aniline has been shown to occur only after prolonged heating at a high temperature.

It is now found that the reaction takes place much more readily in the presence of a catalytic agent, such as copper, nickel, cobalt, or any other heavy metal, its oxide, or salt.

Under these conditions, sodium reacts with aniline at 140°; the reaction also takes place with *o*-toluidine or methylaniline; the products are hygroscopic, fairly-stable substances, but are decomposed by water into sodium hydroxide and original base. F. M. G. M.

Preparation of Cerium Phenoxides. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 214782).—The compounds formed by the interaction of cerium salts with phenolic compounds have similar disinfectant properties to the bismuth phenoxides, but are less toxic and irritating than the phenols themselves.

Cerium phenoxide, prepared from cerium nitrate, phenol, and sodium hydroxide, is pale brown, odourless, and insoluble in water; it contains 31% cerium.

Cerium o-*methoxyphenoxide* analogously prepared is pink, insoluble in water, but soluble in alcohol, chloroform, or ether.

Cerium β-naphthoxide has similar properties, and contains 30% of cerium. F. M. G. M.

Behaviour of Phenyl Sulphide towards Hydrogen Peroxide. Oscar Hinsberg (*Ber.*, 1910, **43**, 289—290).—When a solution of phenyl sulphide in glacial acetic acid is treated with the equivalent quantity

of hydrogen peroxide at the ordinary temperature, phenyl sulphoxide is formed (compare Abstr., 1908, i, 875). If, however, an excess (more than 2 gram-molecules) of hydrogen peroxide is used, and the mixture kept at the room temperature, crystals of phenylsulphone begin to form after a few days. The quantity of sulphone is increased by precipitation with water. Phenylsulphoxide could not be detected in the reaction mixture.

If acetone is used as the solvent (compare Smiles and Gazdar, Trans., 1908, **93**, 1833) there is no action between phenyl sulphide and hydrogen peroxide at the ordinary temperature. Reaction only takes place after heating for an hour in a sealed tube at 80—100°, and even in the presence of excess of hydrogen peroxide, only phenyl sulphoxide is formed.

It is assumed that when glacial acetic acid is used as the solvent, it takes part in the reaction, owing to the formation of peracetic acid, $CH_3\cdot CO\cdot O\cdot OH$. T. S. P.

p-Tolyl Trisulphide. BROR HOLMBERG (*Ber.*, 1910, **43**, 226—227).—The author has shown previously (Abstr., 1908, i, 308) that the mercaptans and thionyl chloride interact, with the formation of disulphide, trisulphide, water, and hydrogen chloride. He now finds that thionylaniline also reacts with mercaptans ; with ethyl mercaptan, thioglycollic acid, and ethyl thioglycollate, the reaction is so violent that the reagents must be diluted with ether or carbon tetrachloride. It is, however, very difficult to isolate pure products from the reaction mixture.

When p-tolyl mercaptan is used, the trisulphide is readily isolated. The mixture of the mercaptan and thionylaniline was heated on the water-bath. After cooling and remaining for a few days, a solid separated, which had m. p. 81—82°, and proved to be p-tolyl trisulphide. It forms small plates, thin prisms, or needles, and is pale yellow. The crude solid was contaminated with a yellow oil, which was a mixture of aniline, p-tolyl disulphide, and aniline sulphate, the latter compound resulting from the hydrolysis of some of the thionylaniline by water formed in the reaction with the mercaptan :

$$4RSH + C_6H_5N{:}SO = R_2S_2 + R_2S_3 + H_2O + C_6H_5\cdot NH_2.$$

The following summary shows that the melting points of the thio-diacetic acids and of the p-tolyl sulphides show a regularity similar to that observed in many homologous series of carbon compounds. However, the member with an uneven number of sulphur atoms has a higher melting point than the next member with an even number.

$S(CH_2\cdot CO_2H)_2$	129°	p-$(C_6H_4Me)_2S$	57°
$S_2(CH_2\cdot CO_2H)_2$	109	p-$(C_6H_4Me)_2S_2$	46
$S_3(CH_2\cdot CO_2H)_2$	124	p-$(C_6H_4Me)_2S_3$	82
$S_4(CH_2\cdot CO_2H)_2$	113	p-$(C_6H_4Me)_2S_4$	75

T. S. P.

Phenanthrene Series. XXVI. Conversion of 9-Chloro-10-hydroxyphenanthrene into other Phenanthrene Derivatives. JULIUS SCHMIDT and HERMANN LUMPP (*Ber.*, 1910, **43**. 423—438).—9-Chloro-10-hydroxyphenanthrene (Abstr., 1909, i, 35) can be used for

the preparation of 3-nitrophenanthraquinone (*loc. cit.*), of 9 : 10-chloro-3-bromohydroxyphenanthrene, and other phenanthrene derivatives.

9(10)-*Chloro*-3-*bromo*-10(9)-*hydroxyphenanthrene*, $C_{14}H_8OClBr$, prepared by the action of a carbon disulphide solution of bromine on 9-chloro-10-hydroxyphenanthrene, forms colourless prisms, m. p. 142°, and dissolves in aqueous solutions of alkalis. Its *acetyl* derivative, $C_{16}H_{10}O_2ClBr$, has m. p. 158—159°, and the *benzoyl* derivative, $C_{21}H_{12}O_2ClBr$, which crystallises in yellow prisms, m. p. 179—180°.

When reduced with zinc dust and glacial acetic acid, the bromo-derivative yields 3-*bromo*-9(10)-*hydroxyphenanthrene*, $C_{14}H_9OBr$, which could not be crystallised on account of the readiness with which it dissolves in most solvents. Its *acetyl* derivative, $C_{16}H_{11}O_2Br$, crystallises in pale yellow prisms, m. p. 135°. The position of the bromine atom in the chlorobromohydroxyphenanthrene follows from the readiness with which it can be oxidised by chromic acid to 3-bromophenanthraquinone (Schmidt and Ladner, *Ber.*, 1905, **37**, 3571), which appears to exist in yellow and reddish-brown chromo-isomerides.

The *dioxime*, $C_{14}H_9O_2N_2Br$, prepared by Schmidt and Söll's method (Abstr., 1907, i, 630), forms green, crystalline aggregates, m. p. 212° (decomp.). The *monosemicarbazone*, $C_{15}H_{10}O_2N_3Br$, forms yellow crystals, m. p. 242° (decomp.), and the *monophenylhydrazone*, $C_{20}H_{13}ON_2Br_2$, has m. p. 177°.

The quinone can be reduced to the quinol by means of phenylhydrazine, but it is difficult to isolate the free dihydroxy-compound. Its acetyl derivative, 3-*bromo*-9 : 10-*diacetoxyphenanthrene*, $C_{18}H_{13}O_4Br$, crystallises in colourless needles, m. p. 177—178°.

3 : 9(10)-*Dihydroxyphenanthrene*, $C_{14}H_8(OH)_2$, formed when the 3-bromo-9(10)-hydroxy-compound is fused at 340° with potassium hydroxide, crystallises in colourless prisms, m. p. 175°. The yield is small.

Fuming nitric acid converts the bromophenanthraquinone into a *dinitro*-derivative, $C_{14}H_5O_6N_2Br_2$, which crystallises in pale yellow, slender needles, m. p. 298°. The *monoxime*, $C_{16}H_6O_6N_3Br$, forms green prisms, m. p. 196° (decomp.); the *semicarbazone*, $C_{15}H_8O_6N_5Br$, forms yellowish-brown prisms, m. p. 272°.

The dinitro-quinone condenses with an alcoholic solution of *o*-phenylenediamine hydrochloride, yielding 3-*bromodinitrophenanthraphenazine*, $C_{20}H_9O_4N_4Br$, as a reddish-white powder, and, when heated on the water-bath with concentrated aqueous ammonia, the quinone yields 3-*bromonitroaminophenanthraquinone*, $NO_2{\cdot}C_{14}H_5BrO_2{\cdot}NH_2$, as a dark brown substance, m. p. 280—282° (decomp.). The *diacetyl* derivative, $C_{18}H_{11}O_6N_2Br$, forms an ochre-yellow powder, m. p. 260° (decomp.).

Reduction of the 3-bromodinitrophenanthraquinone with tin and concentrated hydrochloric acid leads to the formation of 3-*chlorodiaminophenanthraquinol*, which can be readily oxidised by atmospheric oxygen to 3-*chlorodiaminophenanthraquinone*, $C_{14}H_5ClO_2(NH_2)_2$. The base can be diazotised readily, and the diazo-solution forms azo-dyes with phenols. The *dioxime*, $C_{14}H_{11}O_2N_4Cl$, forms a deep bluish-black powder, m. p. 264° (decomp.). When the diamino compound is diazo-

tised and the solution boiled, *3-chlorodihydroxyphenanthraquinone*, $C_{14}H_5ClO_2(OH)_2$, is obtained as a dark red powder, which is not a substantive dye. The *acetyl* derivative, $C_{18}H_{11}O_6Cl$, forms brownish-red crystals, m. p. 245°. J. J. S.

Preparation of Carbonateguaiacol-5-sulphonic Acid and its Salts. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 215050. Compare Abstr., 1909, i, 789).—The preparation of carbonatoguaiacol-5-sulphonic acid and its salts by the action of concentrated sulphuric acid on guaiacol carbonate has been described previously. The free acid forms colourless to dark red, hygroscopic crystals; its cold aqueous solution gives no colour with ferric chloride, but, on heating, carbon dioxide is evolved.

Potassium carbonatoguaiacol-5-sulphonate crystallises in needles, has a neutral reaction, gives no colour with ferric chloride, but by prolonged boiling of its aqueous solution is decomposed into potassium guaiacol-5-sulphonate with evolution of carbon dioxide.

F. M. G. M.

Hydroxyphenylalkylamines and Dihydroxyphenylalkylamines. CARL MANNICH and W. JACOBSOHN (*Ber.*, 1910, **43**, 189—197. Compare Rosenmund, this vol., i, 106; Barger, Trans., 1909, **95**, 1123, 2193).—Homologues of *p*-hydroxyphenylamine have been obtained by reducing aldoximes or ketoximes to bases of the type $OMe\cdot C_6H_4\cdot CH_2\cdot CHR\cdot NH_2$ or $C_6H_3(OMe)_2\cdot CH_2\cdot CHR\cdot NH_2$, and converting these by heating with hydriodic acid into the corresponding phenolic amines. The ketones selected were *p*-methoxybenzyl methyl ketone, 3 : 4-methylenedioxybenzyl methyl ketone, and 3 : 4-dimethoxybenzyl methyl ketone; the aldehydes were *p*-methoxyphenylacetaldehyde and 3 : 4-dimethoxyphenylacetaldehyde.

To obtain *p*-methoxybenzyl methyl ketone, b. p. 136—140°/12 mm., anethole was converted into the dibromide, and this into the bromohydrin, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CHMeBr$, which on heating with alcoholic potassium hydroxide gave anetholoxide; this, on heating at 220°, undergoes rearrangement to the ketone, $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$. The oxime, on reduction with sodium amalgam in acetic acid solution, forms p-*methoxyphenyl*iso*propylamine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NH_2$, a colourless, strongly alkaline oil, b. p. 158°/25 mm.; the *hydrochloride* forms large, colourless crystals, m. p. 210°.

p-*Hydroxyphenyl*iso*propylamine* crystallises in colourless rosettes, m. p. 125—126°; the *hydriodide* has m. p. 155°.

iso*Eugenol methyl ether bromohydrin*, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CHMeBr$, has m. p. 78°. It yields the oxide already described by Fourneau and Tiffeneau (Abstr., 1905, i, 591), which readily undergoes rearrangement to 3 : 4-dimethoxybenzyl methyl ketone, b. p. 198°/20 mm.

3 : 4-*Dimethoxyphenyl*iso*propylamine* is an almost colourless oil, b. p. 166—168°/20 mm.; the *hydrochloride* has m. p. 144°. 3 : 4-*Dihydroxyphenyl*iso*propylamine*, $C_6H_3(OH)_2\cdot CH_2\cdot CHMe\cdot NH_2$, yields a *hydrochloride*, m. p. 190—192°.

3 : 4-*Methylenedioxyphenyl*iso*propylamine* is a colourless oil, m. p. 157°/22 mm.; the hydrochloride has m. p. 180—181°.

Homoanisaldehyde, $OMe\cdot C_6H_4\cdot CH_2\cdot CHO$, is conveniently prepared by oxidation of *p*-methoxystyrene with mercury oxide and iodine; the oxime forms prisms, m. p, 120° (compare Rosenmund, this vol., i, 106).

The *oxime* of homoveratraldehyde crystallises in prisms, m. p. 90—91°; the *oxime* of veratraldehyde has m. p. 82°. On reduction, the oxime yields 3 : 4-*dimethoxyphenylethylamine*, a faintly yellow-coloured oil, b. p. 188°/15 mm.; the *hydrochloride* has m. p. 154—155°.

3 : 4-*Dihydroxyphenylethylamine*, $C_6H_3(OH)_2\cdot CH_2\cdot CH_2\cdot NH_2$, forms a crystalline hydrochloride, decomp. 220°; it shows a green coloration with ferric chloride. E. F. A.

Quinocarbonium Perchlorates (II) and the Solvent Action of Chlorinated Ethanes. KARL A. HOFMANN, HEINZ KIRMREUTHER, and A. THAL (*Ber.*, 1910, **43**, 183—188. Compare this vol., i, 3).—The triphenylcarbinyl perchlorates crystallise so well that pure preparations are readily obtained from impure carbinols. In accordance with their intense colour, they are easily ionised, so that in solvents such as tetrachloroethane, which is unable to dissociate triphenylmethyl chloride, they still conduct the electric current.

Aurin perchlorate forms doubly refractive, four-sided prisms, which in direct light are orange-red with a light blue reflex. *p*-Trianisylcarbinol perchlorate (compare Gomberg and Cone, this vol., i, 55) crystallises in cinnabar-red, flat needles. It is relatively stable towards water.

Triphenylcarbinyl perchlorate dissolves with a reddish-yellow coloration in tetrachloroethane, and tri-*p*-anisylcarbinol perchlorate with an intense orange coloration. Both solutions conduct electricity, likewise those of the perchlorates in ethylene chloride.

The solubility of the perchlorates in a number of solvents has been compared by the intensity of the colour produced in the saturated solution. The solvents take the following order, the more highly coloured coming first: ethylene chloride, tetrachloroethane, chloroform, dichloroethylene, pentachloroethane, trichloroethylene, perchloroethylene, carbon tetrachloride. The last two or three solvents only become coloured when boiled with the perchlorate. Mercuric chloride dissolves in these solvents in precisely the same order, the solubility being greatest in ethylene chloride and almost nothing in carbon tetrachloride. This confirms the view that the perchlorates are of the nature of metallic salts.

The solvents dissolve sulphur in an altogether different order, ethylene chloride being the least, perchloroethylene the most, effective solvent. E. F. A.

Action of α-Bromonaphthalene and Magnesium on Certain Carbonyl Compounds. E. SCHURAKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1687—1694).—The interaction of α-bromonaphthalene, magnesium, and acetone yields the compound $MgBr\cdot O\cdot CMe_2\cdot C_{10}H_7$,

which is decomposed by water, giving α-naphthyldimethylcarbinol (compare Grignard, Abstr., 1901, i, 393). When heated with anhydrous oxalic acid, this alcohol yields β-naphthylpropylene (Grignard, *loc. cit.*), b. p. 251—251·5°/744 mm., D_4^{25} 1·0078, n^{25} 1·60684; the molecular refraction, calculated according to the Lorenz and Lorentz formula, is 57·554, which, as is often the case with naphthalene derivatives, differs considerably from the calculated value, 55·387.

p-*Tolyl-α-naphthylmethylcarbinol*, $C_6H_4Me{\cdot}CMe(C_{10}H_7){\cdot}OH$, prepared from α-bromonaphthalene, magnesium, and tolyl methyl ketone, was obtained as a dark viscous, impure mass. When heated with anhydrous oxalic acid, this alcohol loses water, giving as-*α-naphthyl*-p-*tolylethylene*, $C_6H_4Me{\cdot}C(C_{10}H_7){:}CH_2$, which is a viscous, faintly yellow liquid, b. p. 224—226°/20 mm., $D_4^{21\cdot5}$ 1·0693, and combines with 2Br per mol.

Anisyl-α-naphthylcarbinol, $OMe{\cdot}C_6H_4{\cdot}CH(C_{10}H_7){\cdot}OH$, prepared from α-bromonaphthalene, magnesium, and anisaldehyde, crystallises in small needles or rhombic prisms, m. p. 87°.

α-Naphthylpropenylcarbinol, $CHMe{:}CH{\cdot}CH(C_{10}H_7){\cdot}OH$, prepared by the interaction of α-bromonaphthalene, magnesium, and crotonaldehyde, is a faintly yellow, viscous liquid, b. p. 204—210°/22 mm.

T. H. P.

Preparation of Nitriles. E. EMMET REID (*Amer. Chem. J.*, 1910, **43**, 162—181).—It was shown by Letts (Abstr., 1872, 1020) that nitriles can be prepared by the action of potassium thiocyanate on organic acids. Krüss (Abstr., 1884, 1314) found in the case of benzonitrile that a better yield could be obtained with lead thiocyanate than with the potassium salt, the reaction being represented by the equation:

$$2C_6H_5{\cdot}CO_2H + Pb(CNS)_2 = 2C_6H_5{\cdot}CN + PbS + H_2S + 2CO_2.$$

In attempting to prepare benzonitrile by Kruss' method, the yield obtained amounted to only 36% of the calculated, and it was observed that only a very small quantity of hydrogen sulphide was evolved. It was therefore considered likely that the hydrogen sulphide might have entered into the reaction and led to the formation of complex products. In order to avoid the formation of hydrogen sulphide, a mixture of lead benzoate and lead thiocyanate was heated, and it was found that, in these circumstances, a much better yield of benzonitrile was obtained. Experiments have been made to ascertain the effect of heating lead, sodium, zinc, and barium benzoates with potassium cyanate, lead cyanate, potassium thiocyanate, lead thiocyanate, barium thiocyanate, lead ferrocyanide, lead cyanide and sulphur, lead ferrocyanide and sulphur, zinc ferrocyanide and sulphur, potassium ferrocyanide and sulphur, and silver cyanide and sulphur. In each case a considerable quantity of benzonitrile was obtained. The results of these experiments are tabulated.

The best method of preparing benzonitrile in the laboratory is to distil a mixture of dry zinc benzoate and dry lead thiocyanate, a yield of 79—91% being thus obtained. A mixture of equivalent quantities of lead ferrocyanide and sulphur may be used instead of the thiocyanate

and, in this case, a yield of about 74% is produced. The formation of the benzonitrile takes place as follows:

$$Zn(CO_2\cdot C_6H_5)_2 + Pb(CNS)_2 = PbS + ZnS + 2CO_2 + 2C_6H_5\cdot CN.$$

On applying this method to other acids, it was found that the nitriles of the three aminobenzoic acids, *p* nitrobenzoic acid, salicylic acid, and phthalic acid, could not be obtained in this way, but that when lead *m*- or *p*-bromobenzoate was distilled with lead thiocyanate, a satisfactory yield of the bromobenzonitrile was produced in each case.

E. G.

Action of Alcoholic Hydrogen Chloride on *m*-Methylnitrosoaminobenzoic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1910, **43**, 206—212. Compare Abstr., 1909, i, 921).—*m*-Aminobenzoic acid in glacial acetic acid is treated with methyl sulphate. After one hour's heating and keeping for twelve hours, the crystals of *m*-aminobenzoic acid sulphate are removed, and the filtrate is treated with sodium nitrite at 0°, whereby m-*methylnitrosoaminobenzoic acid*, $NO\cdot NMe\cdot C_6H_4\cdot CO_2H$, m. p. 179—180° (bath previously at 160°), is obtained, which separates, slightly impure, from water in blood-red leaflets, and is converted after two weeks by alcoholic hydrogen chloride into *ethyl* m-*methylaminobenzoate hydrochloride*, m. p. 137° (corr.), which is converted into *ethyl* m-*methylnitrosoaminobenzoate*, m.p. 32°, by nitrous acid at 0°. After twenty-four hours, *m*-methylnitrosoaminobenzoic acid and alcoholic hydrogen chloride yield m-*methylaminobenzoic acid hydrochloride*, $CO_2H\cdot C_6H_4\cdot NHMe,HCl$, m. p. 244°, which is converted by *N*-sodium hydroxide into *m*-methylaminobenzoic acid, m. p. 127° (corr.).

C. S.

New Drugs. V. ALFRED EINHORN (*Annalen*, 1910, **371**, 125—131. Compare Abstr., 1900, i, 439, 493; 1903, i, 257; 1908, i, 312).—Mainly a résumé of the work which led to the preparation of novocaine (ω-diethylaminoethyl *p*-aminobenzoate hydrochloride: compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923). As far as can be ascertained, all soluble aromatic esters, with the apparent exception of α-cocaine (compare Willstätter, Abstr., 1896, i, 707), are capable of producing local anæsthesia to a greater or less degree. Generally speaking, the anæsthetic action is destroyed by the introduction of a carboxyl or sulphoxyl group into the molecule; other substituents, such as halogen, hydroxyl, alkoxyl, nitro, amino, etc., either increase or diminish, but never destroy completely, the activity of an aromatic ester.

W. H. G.

Diethylaminoethyl and Piperidinoethyl *p*-Aminobenzoates. ALFRED EINHORN and EMIL UHLFELDER (*Annalen*, 1910, **371**, 131—142).—An account of the preparation of diethylaminoethyl *p*-aminobenzoate (novocaine), piperidinoethyl *p*-aminobenzoate, and some derivatives of these esters, much of which has appeared already (compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923; 1908, i, 638).

Diethylaminoethyl *p*-aminobenzoate crystallises with $2H_2O$ in small needles, m. p. 51°; the anhydrous substance crystallises in plates, m. p. 61°; the following derivatives have been prepared: *mercuri-*

chloride, needles, m. p. 139°; *hydriodide*, small needles, m. p. 121—122°; *mercuri-iodide*, $C_{13}H_{20}O_2N_2,HI,HgI_2$, small, white needles, m. p. 127°; *nitrate*, needles, m. p. 100—101°; *argentonitrate*, needles, m. p. 107°; *sulphate*, prisms, m. p. 170°; *chlorate*,

$$C_{13}H_{20}O_2N_2,HClO_3,$$

needles, m. p. 89°; *borate*, $C_{13}H_{20}O_2N_2,4B(OH)_3$, small needles, m. p. 159—160°; *trichloroacetate*, prisms, m. p. 89°; *thiocyanate*, prisms, m. p. 83°; *phthalate*, prisms, m. p. 119°; *ethochloride*,

$$NH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_3Cl,H_2O,$$

prisms, sinters at 135°, and is completely molten at 180°; the anhydrous ethochloride has m. p. 198° (decomp.); *acetyl* derivative, a viscid oil, the *hydriodide* of which, $C_{15}H_{22}O_3N_2,HI$, crystallises in small rosettes, m. p. 146—147; the *hydrochloride* of the *benzoyl* derivative,

$$C_{20}H_{24}O_3N_2,HCl,$$

forms small needles, m. p. 189°; the p-*nitrobenzoyl* derivative crystallises in small needles, m. p. 129—130°, and when reduced yields the corresponding p-*aminobenzoyl* derivative, small needles, m. p. 124°, the *hydrochloride* of which, $C_{20}H_{25}O_3N_3,HCl$, crystallises in needles, m. p. 221°.

Piperidinoethyl p-*acetylaminobenzoate*, $C_{16}H_{22}O_3N_2$, crystallises in needles, m. p. 86—87°; the *hydrochloride* has m. p. 228°; the ester is converted by a hot alcoholic solution of hydrogen chloride into the *dihydrochloride* of piperidinoethyl *p*-aminobenzoate, m. p. 225°.

W. H. G.

Alkylaminoalkyl *p*-Aminobenzoates. ALFRED EINHORN, KARL FIEDLER, CARL LADISCH, and EMIL UHLFELDER (*Annalen*, 1910, **371**, 142—161).—The compounds described in this paper were prepared subsequently to novocaine, but not one of them is more suitable than this substance for the purpose of producing local anæsthesia. They are all obtained by the reduction of the corresponding *p*-nitrobenzoates, which are prepared by the action of *p*-nitrobenzoyl chloride on the requisite alkamine.

Dimethylaminoethyl p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NMe_2,$$

prepared by heating dimethylaminoethyl alcohol with *p*-nitrobenzoyl chloride at 130°, crystallises in slender, matted needles, m. p. 58—59°; when reduced with tin and hydrochloric acid, it yields the corresponding *amino*-compound, $C_{11}H_{16}O_2N_2$, crystallising in large prisms, m. p. 121°, the *hydrochloride* of which, $C_{11}H_{16}O_2N_2,HCl$, forms small, slender needles, m. p. 185—186°.

Diisopropylaminoethyl p-*nitrobenzoate* is an oil; the *hydrochloride*, $C_{15}H_{22}O_4N_2,HCl$, crystallises in small needles, m. p. 136·5°; the corresponding *amino*-compound, $C_{15}H_{24}O_2N_2$, crystallises in slender needles, m. p. 48°, and forms a *hydrochloride*, crystallising in prisms, m. p. 195°.

Diisobutylaminoethyl p-*nitrobenzoate* is an oil; the *hydrochloride*, $C_{17}H_{26}O_4N_2,HCl$, forms slender, felted needles, m. p. 160—161°; the *amino*-compound, $C_{17}H_{28}O_2N_2$, small, slender needles, m. p. 84—85°, forms a *hydrochloride*, which crystallises in prisms, m. p. 195—196°.

Diisoamylaminoethyl p-*nitrobenzoate* is an oil; the *hydrochloride*,

$C_{19}H_{30}O_4N_2$,HCl, crystallises in small needles, m. p. 123—124°; the *amino*-compound, $C_{19}H_{32}O_2N_2$, leaflets, m. p. 44—45°, forms a *hydrochloride*, crystallising in needles, m. p. 154°.

Diethylaminomethylmethylethylcarbinol, $NEt_2{\cdot}CH_2{\cdot}CMeEt{\cdot}OH$, prepared by the action of diethylamine on the corresponding chloro-compound, is an oil, b. p. 71—73°/15·5 mm.; the p-*nitrobenzoate* is an oil, the *hydriodide* of which, $C_{16}H_{24}O_4N_2$,HI, forms pale yellow crystals, m. p. 167°; the p-*aminobenzoate* is a pale yellow oil, the *picrate* of which, $C_{22}H_{29}O_9N_5$, is a pale yellow, crystalline powder, m. p. 121°.

Piperidinomethylmethylethylcarbinol, $NC_5H_{10}{\cdot}CH_2{\cdot}CMeEt{\cdot}OH$, is a colourless oil, b. p. 101—104°/18 mm.; the p-*nitrobenzoate* is a viscid, yellowish-brown oil, the *hydriodide* of which, $C_{17}H_{24}O_4N_2$,HI, crystallises in yellow leaflets, m. p. 190°; the p-*aminobenzoate* is an oil, crystalline salts of which could not be obtained.

Diethylaminomethylethylcarbinol has b. p. 197—200° (compare Paal and Weidenkaff, Abstr., 1906, i, 236); the p-*nitrobenzoate* is an oil, the *hydriodide* of which, $C_{17}H_{26}O_4N_2$,HI, crystallises in yellow prisms, m. p. 154°; the *hydrochloride* of the oily p-*aminobenzoate*, $C_{17}H_{28}O_2N_2$,HCl, forms rhomboidal crystals, m. p. 166—167°.

*Tetraethyldiamino*iso*propyl* p-*nitrobenzoate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH(CH_2{\cdot}NEt_2)_2,$$

forms yellow crystals, m. p. 41°; the *dihydrochloride* crystallises in slender, felted needles, m. p. 198°; the p-*aminobenzoate*, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 50°; the *dihydrochloride* forms faintly yellow, slender needles, m. p. 222°.

*Dipiperidino*iso*propyl* p-*nitrobenzoate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH(CH_2{\cdot}NC_5H_{10})_2,$$

is an oil; the *dihydriodide* crystallises in lemon-yellow, slender needles, m. p. 232°; the corresponding *amino*-compound, $C_{20}H_{31}O_2N_3$, forms colourless prisms, m. p. 137·5°, the *dihydrochloride* of which crystallises in slender needles, m. p. 261°.

The p-*nitrobenzoate* of α-diethylaminopropane-βγ-diol,

$NEt_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_4{\cdot}NO_2$ or

$$NEt_2{\cdot}CH_2{\cdot}CH(CO_2{\cdot}C_6H_4{\cdot}NO_2){\cdot}CH_2{\cdot}OH,$$

is an oil; the *hydrochloride* is a microscopic, crystalline powder, m. p. 152°; the corresponding *amino*-ester is an oil; the *di*-p-*nitrobenzoate*, $C_{21}H_{23}O_8N_3$, forms small, yellow needles, m. p. 90—92°; the *di*-p-*aminobenzoate* has m. p. 132°; the *hydrochloride*, $C_{21}H_{27}O_4N_3$,HCl, is a crystalline powder, m. p. 185°. The p-*nitrobenzoate* of the corresponding piperidino-compound, $C_{15}H_{20}O_5N_2$, forms leaflets, m. p. 60—63°; the *hydrochloride* crystallises in white needles, m. p. 212°; the p-*aminobenzoate*, $C_{15}H_{22}O_3N_2$, crystallises in prisms, m. p. 91°; the *hydrochloride* forms white needles, m. p. 206°; the *di*-p-*nitrobenzoate*, $C_5NH_{10}{\cdot}CH_2{\cdot}CH(CO_2{\cdot}C_6H_4{\cdot}NO_2){\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_4{\cdot}NO_2$, crystallises in pale, yellow prisms, m. p. 108°; the *di*-p *aminobenzoate* crystallises in prisms, m. p. 127°; the *hydrochloride*, $C_{22}H_{27}O_4N_3$,HCl, forms small needles, m. p. 210·5°. W. H. G.

Esters and Alkylamino-esters of 3 : 4-Diaminobenzoic Acid. ALFRED EINHORN and EMIL UHLFELDER (*Annalen*, 1910, **371**, 162—179. Compare Einhorn, Abstr., 1908, i, 639).—The compounds

described in this paper were prepared with the object of obtaining derivatives of alkyl 3 : 4-diaminobenzoates yielding salts with a neutral reaction, which could consequently be employed as anæsthetics. The esters of 3 : 4-diaminobenzoic acid when boiled with organic acids yield esters of 2-alkylbenziminazole-5-carboxylic acid, and when treated with acetyl chloride yield the corresponding dichloroacetyl derivatives ; the latter substances interact with secondary bases, for example, piperidine, yielding the dipiperidinoacetyl compounds.

Methyl 2-methylbenziminazole-5-carboxylate,

$$\begin{array}{l} C(CO_2Me)\cdot CH:C-N \\ \| \qquad\qquad\qquad\quad | \\ CH\text{———}CH:C\cdot NH \end{array}\!\!>\!CMe$$

crystallises in needles, m. p. 172°; the *hydrochloride* forms small needles, m. p. 257° ; the *ethyl* ester crystallises in needles, m. p. 180°. *Methyl 2-ethylbenziminazole-5-carboxylate*, $C_{11}H_{12}O_2N_2$, crystallises in needles, m. p. 141° ; the *hydrochloride* has m. p. 252°. The *dibenzoyl* derivative of methyl 3 : 4-diaminobenzoate, $C_{22}H_{18}O_4N_2$, crystallises in small, white needles, m. p. 231° ; the *dichloroacetyl* derivative,

$$CO_2Me\cdot C_6H_3(NH\cdot CO\cdot CH_2Cl)_2,$$

forms needles, m. p. 177° ; the *dipiperidinoacetyl* derivative,

$$CO_2Me\cdot C_6H_3(NH\cdot CO\cdot CH_2\cdot NC_5H_{10}),$$

has m. p. 108°.

Ethyl 3-nitro-4-chloroacetylaminobenzoate, $C_{11}H_{11}O_5N_2Cl$, crystallises in small, yellow needles, m. p. 102°. *Ethyl 3-nitro-4-piperidinoacetylaminobenzoate* crystallises in yellow needles, m. p. 70—71°, and when reduced with tin and hydrochloric acid below 35° yields the corresponding *amino*-compound, $C_{16}H_{23}O_3N_3$, small needles, m. p. 103°, the *hydrochloride* of which crystallises in leaflets, m. p. 204°, whilst at a higher temperature it is converted into *ethyl 2-piperidinomethylbenziminazole-5-carboxylate*, $C_{16}H_{21}O_2N_3$, an oil, the *dihydrochloride* of which crystallises in needles, m. p. 227°. The following compounds are similarly prepared : *ethyl 3-nitro-4-diethylglycylaminobenzoate*,

$$NEt_2\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3(NO_2)\cdot CO_2Et,$$

yellow needles, m. p. 71°; *ethyl 3-amino-4-diethylglycylaminobenzoate*, small needles, m. p. 64° ; *hydrochloride*, needles, m. p. 194° ; *ethyl 2-diethylaminomethylbenziminazole-5-carboxylate*, $C_{15}H_{21}O_2N_3$, pointed needles, m. p. 67° ; *hydrochloride*, small needles, m. p. 173° ; *dihydrochloride*, m. p. 199°.

Chloroethyl 3 : 4-diaminobenzoate, $C_6H_3(NH_2)_2\cdot CO_2\cdot CH_2\cdot CH_2Cl$, is obtained by acting on a mixture of 3 : 4-diaminobenzoic acid and ethylene chlorohydrin with hydrogen chloride in the presence of a small quantity of concentrated sulphuric acid; it crystallises in needles, m. p. 80°, and, when heated with diethylamine under pressure at 100—120°, yields the corresponding *diethylaminoethyl* ester, an oil, the *hydrochloride* of which, $C_{13}H_{21}O_2N_3$,HCl, forms needles, m. p. 163° ; the *picrate* crystallises in yellow needles, m. p. 189—190°. The diethylaminoethyl ester undergoes the following changes: (1) with glyoxal, it yields *diethylaminoethyl quinoxaline-6-carboxylate*, an oil, the *hydrochloride* of which, $C_{15}H_{21}O_2N_3$,HCl, crystallises in needles, m. p. 187° ; (2) when treated with sodium nitrite and hydrochloric acid, it yields *diethylaminoethyl 3 : 4-aziminobenzoate hydrochloride*, $C_{13}H_{18}O_2N_3$,HCl, small needles, m. p. 150—151° ; (3) it condenses

with *p*-dimethylaminobenzaldehyde, yielding a *substance*, which crystallises in yellow needles, m. p. 161°, and with benzaldehyde, yielding an oily *substance*, the *hydrochloride* of which crystallises in prisms, m. p. 190°.

Piperidinoethyl 3 : 4-*diaminobenzoate* crystallises in needles, m. p. 103°; when heated with glacial acetic acid, it yields *piperidinoethyl* 2-*methylbenziminazole*-5-*carboxylate*, $C_{16}H_{21}O_2N_3$, needles, m. p. 159—160°, the *hydrochloride* and *dihydrochloride* of which crystallise in needles, m. p. 162—163° and 262° respectively.

Diethylaminoethyl 3-*nitro*-4-*dimethylaminobenzoate*, prepared from 3-nitro-4-dimethylaminobenzoic acid and diethylaminoethanol, is an oil; the corresponding *amino*-compound, also an oil, forms a *hydrochloride*, $C_{15}H_{25}O_2N_3,HCl$, which crystallises in needles, m. p. 164°.

Methyl 3 : 4-*tetramethyldiaminobenzoate dihydriodide*, prepared by heating methyl 3-amino-4-dimethylaminobenzoate with methyl iodide and methyl alcohol under pressure at 100°, crystallises in needles, m. p. 109—110°; the *dihydrobromide*, $C_{12}H_{18}O_2N_2,2HBr$, crystallises in needles, m. p. 205°; the correspondiug *diethylaminoethyl* ester is an oil; the *hydrochloride*, $C_{17}H_{29}O_2N_3$, crystallises in small, white needles, m. p. 140—141°. W. H. G.

Isomerism of Anils (Schiff's Bases). OTTO ANSELMINO (*Ber.*, 1910, **43**, 462—463. Compare Manchot and Furlong, Abstr., 1909, i, 805; this vol., i, 33; Anselmino, Abstr., 1906, i, 13; 1907, i, 913; Knoevenagel and Schrötter, Abstr., 1905, i, 64).—Polemical. J. J. S.

Differences between Cinnamic Acid from Storax and Synthetical Cinnamic Acid. C. N. RIIBER and V. MORITZ GOLDSCHMIDT (*Ber.*, 1910, **43**, 453—462. Compare E. Erlenmeyer, jun., Abstr., 1907, i, 318; 1909, i, 156, 647, 648).—Although cinnamic acid from storax differs so materially in habit from the synthetical acid, it is shown that the characteristic crystallographic constants are the same for the two acids. The chief differences are (*a*) the extremely thin plates in which the synthetical acid crystallises; (*b*) the absence of definite faces in the crystals of the synthetical acid; the plates as a rule have a crinkled edge.

As the synthetical acid when repeatedly crystallised approaches the habit of the storax acid, the conclusion is drawn that the former acid is identical with the storax acid, but contains a small amount of an impurity which is gradually removed by repeated crystallisation. The presence of this impurity retards to an enormous extent the development of the crystals in the direction normal to the face *b*{010}.

By careful fractionation of the ethyl ester of the synthetical acid, it has been found possible to isolate a fraction b. p. about 120°/0·2 mm., which when hydrolysed gives an acid containing about 9% Cl. This acid is probably an impure chlorocinnamic acid, and it is shown that when this impure acid or when small amounts of either *o*- or *p*-chlorocinnamic acids are added to the acid from storax, they alter its crystalline habit and transform it into the characteristic crystals of the synthetical acid. The synthetical acid is thus the same

acid as that from storax, but contains a small amount of a chloro-acid which completely alters its crystalline appearance.

Erlenmeyer's hetero-acid contains a larger proportion of the chloro-acid than does the synthetical acid.

Erlenmeyer states that specimens of benzaldehyde which are free from chlorine yield the synthetical acid. It is shown that small amounts (0·3%) of *o*-nitrocinnamic acid have the same effect on the crystalline habit of the storax acid as larger amounts of the chloro-acids.

Erlenmeyer's α- and β-cinnamic acids are regarded as dimorphous forms (compare Lehmann, *Zeitsch. Kryst. Min.*, 1885, **10**, 329).

J. J. S.

Transformations of *allo*-Cinnamic and *iso*Cinnamic Acids. CARL LIEBERMANN and H. TRUCKSÄSS (*Ber.*, 1910, **43**, 411—414. Compare this vol., i, 36).—It is shown that when *allo*cinnamic or *iso*cinnamic acid of m. p. 58° is crystallised from carefully rectified light petroleum (b. p. 30—40°), crystals of the *iso*-acid, m. p. 42°, can usually be obtained if proper precautions are taken. The method consists in introducing a comparatively dilute solution of the acid into a glass tube by means of a suitable funnel, and then boiling the solution for some little time, so that the walls of the tube are thoroughly purified, and also that the solution may be concentrated. The tube is then sealed, and when placed in ice-cold water or in a freezing mixture, crystals of the acid m. p. 42° separate. These occasionally become transformed into the less fusible acids during transference from the tube. J. J. S.

Mechanism of the Transformation of α-Hydroxy-$\beta\gamma$-unsaturated Acids into the Isomeric γ-Keto-acids. EMIL ERLENMEYER (*Festschrift Otto Wallach*, 1909, 404—413).—A discussion on the course of the intramolecular rearrangement of α-hydroxy-$\beta\gamma$-unsaturated acids into γ-ketones (compare Fittig, Abstr., 1897, i, 14; 1898, i, 196), based on the author's investigations (compare Abstr., 1898, i, 668; 1903, i, 32, 414; 1904, i, 500, 892, 1025). W. H. G.

[Preparation of Triphenylmethane Colouring Matters from Diortho-substituted Benzaldehydes.] ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 213502. Compare Abstr., 1908, i, 986).—It has been shown previously that the diortho-substituted benzaldehydes when employed in the production of triphenylmethane dyes yield colours of remarkable depth and fastness; it is now found that these properties are enhanced when the two ortho-substituents consist of different halogen atoms. The following new aldehydes are described:

2-*Chloro*-6-*bromobenzaldehyde*, prepared from 2-chloro-6-bromotoluene, forms colourless, spear-shaped crystals, m. p. 68°.

2-*Chloro*-4 : 6-*dibromo*-5-*aminobenzaldehyde*, m. p. 124°, a colourless, crystalline powder, is obtained by the bromination in aqueous suspension of 2-chloro-5-aminobenzaldehyde. 2 : 4 : 6-*Tribromo* 5-*aminobenzaldehyde*, m. p. 136—137°. 2-*Chloro*-4 : 6-*dibromo*-5-*hydroxybenzaldehyde* crystallises in dark yellow needles, and has m. p. 116°.

F. M. G. M.

p-Methoxysalicylaldehyde. PAUL FRIEDLÄNDER (*Monatsh.*, 1909, **30**, 879—881).—Since p-methoxysalicylaldehyde (o-hydroxyanisaldehyde), prepared by the action of sodium hydroxide on 4-methoxy-2-keto-1-indoxylbenzene (compare Friedländer and Schuloff, Abstr., 1908, i, 674), did not have the properties of the o-hydroxyanisaldehyde described by Tiemann and Parrisius (compare Abstr., 1881, 270), the compound has been prepared by the method employed by these investigators, also by the action of methyl sulphate on 2 : 4-dihydroxybenzaldehyde, and found to be identical with that derived from 4-methoxy-2-keto-1-indoxylbenzene. It is shown, further, that the substance obtained by Goulding and Pelly from *Chlorocodon Whiteii* (Proc., 1908, **24**, 62) is o-hydroxyanisaldehyde.

o-Hydroxyanisaldehyde has m. p. 41°; the oxime has m. p. 138°; the phenylhydrazone has m. p. 138°; the *aldazine*,

$$[OMe\cdot C_6H_3(OH)\cdot CH:N-]_2,$$

forms small, greenish-yellow crystals, m. p. 220°. W. H. G.

Orthovanillin [2-Hydroxy-3-methoxybenzaldehyde] and its Derivatives. FRANCIS A. M. NOELTING (*Bull. Soc. Ind. Mulhouse*, 1909, **79**, 401—430).—The compound described by Tiemann and Koppe as β-m-methoxysalicylaldehyde (compare Abstr., 1882, 54) is definitely shown to be 2-hydroxy-3-methoxybenzaldehyde, for, when treated with acetic anhydride, it yields 8-methoxycoumarin.

A large number of hydroxy- and methoxy-derivatives of benzaldazine and benzylideneaniline have been prepared with the object of ascertaining the effect of these groups on the colour of the substance. It is found that the para-derivatives of benzaldazine are the most highly-coloured, whilst the ortho-substitution products of benzylideneaniline are more intensely coloured than the corresponding paraisomerides; for example, vanillaldazine is golden-yellow, whilst 2-hydroxy-3-methoxybenzyaldazine is lemon-yellow; 2-hydroxy-3-methoxy benzylideneaniline is orange, whilst the 4-hydroxy-isomeride is pale yellow. The ortho-, meta-, and para-hydroxy-derivatives of benzylideneaniline are lemon-yellow, white, and pale yellow respectively; the methyl ethers are all colourless, although the hydrochlorides are lemon-yellow; the methoxy-derivatives of the methyl ethers are not coloured, although the introduction of a methoxy-group into the hydroxy-derivatives increases the colour. Derivatives of benzylideneaniline containing a hydroxy- or methoxy-group are rendered more intensely coloured by the introduction of a hydroxy-group.

2-Hydroxy-3-methoxybenzaldehyde crystallises in pale yellow needles, m. p. 45·5°, b. p. 265—266°; it dyes wool an intense yellow, and silk a pale yellow; the m. p.'s of various mixtures of this compound with vanillin are recorded; the *sodium* salt, $C_8H_7O_3Na,H_2O$, crystallises in lemon-yellow plates; the *benzoate* crystallises in small, white needles, m. p. 74—75°; the *oxime* crystallises in white needles; the *phenylhydrazone*, $OMe\cdot C_6H_3(OH)\cdot CH:N\cdot NHPh$, forms colourless needles, m. p. 130—131°; the *phenylmethylhydrazone* forms colourless crystals, m. p. 62°. The *methyl ether*, $C_6H_3(OMe)_2\cdot CHO$, crystallises in white needles, m. p. 52—53°, and dissolves in concentrated sulphuric acid to a blood-red solution; the finely-divided substance produces

violent sneezing; the *oxime* has m. p. 98—99°; the *phenylhydrazone*, m. p. 138°, is white. The parent substance couples with diazo-compounds, forming compounds of the type $\begin{matrix}C(CHO){:}CH — C{\cdot}N_2R \\ \vert \qquad\qquad\qquad \Vert \\ C(OH){:}C(OMe){\cdot}CH\end{matrix}$, and forms *condensation products* with the following bases, the colours of which only are given: α-naphthylamine, scarlet; β-naphthylamine, crimson; *p*-toluidine, orange; *p*-anisidine, yellowish-orange; *p*-phenetidine, yellowish-orange; *o*-chloroaniline, bright red; dichloroaniline, bright red; *p*-nitroaniline, orange-red; *m*-nitrotoluidine, orange-yellow; *p*-phenylenediamine, scarlet; benzidine, brick-red.

o-*Methoxybenzylideneaniline*, m. p. 44°, is white; the *meta*-isomeride is also white; 3 : 4-*dihydroxybenzylideneaniline*, m. p. 172°, is bright yellow, whilst the *dimethyl ether*, m. p. 81°, is white; 2-*hydroxy*-3-*methoxybenzylideneaniline*, m. p. 84—85°, is orange, whilst the *methyl ether*, m. p. 82·5°, is white; 4-*hydroxy*-3-*methoxybenzylideneaniline*, m. p. 152—153°, is pale yellow.

m-*Hydroxybenzaldazine*, m. p. 204—205°, is pale yellow; 2-*hydroxy*-3-*methoxybenzaldazine*, m. p. 198—199°, is lemon-yellow, whilst the *methyl ether*, m. p. 151°, is pale yellow.

Dimethylaniline condenses with 2-hydroxy-3-methoxybenzaldehyde and 2 : 3-dimethoxybenzaldehyde, yielding 4′ . 4″-*tetramethyldiamino*-2‴-*hydroxy*-3‴-*methoxytriphenylmethane*, m. p. 144°, and 4′ : 4″-*tetramethyldiamino*-2‴ : 3‴-*dimethoxytriphenylmethane*, m. p. 130—131°, respectively; the *hydrochlorides* are green and bluish-green respectively.

8-*Methoxycoumarin* forms inodorous, white crystals, m. p. 89°.

W. H. G.

Carbonyl Group in the Nascent State. Pavel Iw. Petrenko-Kritschenko (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1698—1703).—A reply to Stewart and Baly (compare Abstr., 1907, i, 220).

T. H. P.

Tetrabromo*cyclo*pentenedione. C. Loring Jackson and H. A. Flint (*Amer. Chem. J.*, 1910, **43**, 135).—Jackson and Russe (Abstr., 1906, i, 290) found that by the action of fuming nitric acid and bromine on tetrabromo-*o*-benzoquinone, two substances were produced, one, yellow, m. p. 142°, and the other, white, m. p. 144—146°. The present investigation was undertaken with a view to the further study of these compounds.

The white substance could not again be obtained, but oxalic acid was invariably produced.

The yellow compound has been found to be identical with Henle's tetrabromo*cyclo*pentene-1 : 3-dione (Abstr., 1907, i, 223), and is shown to have the constitution $CO{<}\begin{matrix}CBr_2{\cdot}CO \\ \vert \\ CBr{=}CBr\end{matrix}$. It is readily decomposed by boiling water or alcohol, but is remarkably stable towards acids or oxidising agents, and can be boiled for several hours with fuming nitric acid without undergoing visible change. When the compound is treated with solution of sodium carbonate for several days at the ordinary temperature, it is converted into dibromomaleic

acid and methylene dibromide. The action of sodium methoxide on the compound also results in the formation of dibromomaleic acid.

By the action of aniline on tetrabromo*cyclo*pentene-1 : 3-dione, there are produced *tribromoanilino*cyclo*pentenedione*, $NHPh\cdot C_5O_2Br_3$, m. p. 178°, which crystallises in yellow needles, and *hydroxyanilinoanil*cyclo*pentenedione*, $NPh\colon C_5O_2(OH)\cdot NHPh$, which forms a dark red, amorphous powder, and does not melt below 300°.

When tetrabromo*cyclo*pentenedione is reduced with sulphurous acid, *dibromodiketo*cyclo*pentene*, $C_5H_2O_2Br_2$, m. p. 151°, is obtained, which crystallises in pale yellow plates, and, on treatment with bromine, is reconverted into tetrabromo*cyclo*pentenedione. Phenylhydrazine reacts with dibromo*cyclo*pentenedione with formation of a brown, amorphous *substance*, which does not melt below 300°. When dibromo*cyclo*pentenedione is treated with aniline, *bromoanilino*cyclo*pentenedione*, $NHPh\cdot C_5H_2O_2Br$, m. p. 121° (decomp.), is produced, which forms slender, yellow needles, and is converted by sodium carbonate solution into 1-*anilino*-Δ^1-cyclo*propen*-3-*one*, $NHPh\cdot C{<}{\overset{CO}{\underset{CH}{|}}}$, m. p. 221° (decomp.), which crystallises in yellow needles.

By the action of methyl alcohol on tetrabromodiketo*cyclo*pentene, *tribromodiketomethoxy*cyclo*pentene*, $OMe\cdot C_5O_2Br_3$, m. p. 67°, is obtained, which forms white, slender needles. The corresponding *ethoxy*-compound, m. p. 110°, crystallises in small, white needles, and is converted by aniline into *hydroxydiketoanilino*cyclo*pentene*,

$$NHPh\cdot C_5H_2O_2\cdot OH,$$

m. p. 140° (decomp.), a red, amorphous substance, which yields an *acetyl* derivative, m. p. 150° (decomp.), as a pale brown, amorphous powder.

E. G.

Nitrosation of the Simplest Cyclic Ketones. WALTHER BORSCHE (*Festschrift Otto Wallach*, 1909, 301—312).—*cyclo*Hexanone is converted by amyl nitrite in the presence of a small quantity of acetyl chloride into 1 : 3-*dioximino*-2-cyclo*hexanone*,

$$CH_2{<}{\begin{matrix}CH_2\cdot C(N\cdot OH)\\ CH_2\cdot C(N\cdot OH)\end{matrix}}{>}CO,$$

which crystallises in glistening, yellow needles, m. p. above 200° (decomp.), and is decomposed by water, alcohol, and dilute acids; the corresponding triketone could not be isolated. The dioxime when treated with an alcoholic solution of sodium ethoxide and benzoyl chloride yields a *substance*, $C_{20}H_{22}O_5N_3$ (?), crystallising in colourless needles, m. p. 92—93°; benzoylation in the presence of pyridine leads to the formation of a *dibenzoate*, $CH_2{<}{\begin{matrix}CH_2\cdot C(OBz)\colon N\\ CH_2\cdot C(OBz)\colon N\end{matrix}}{>}CO$ (?), which crystallises in slender, yellow needles, m. p. 170—172° (decomp.), and when boiled with an aqueous solution of sodium hydroxide is probably decomposed, thus: $C_{20}H_{16}O_5N_2 + 4NaOH = CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN + Na_2CO_3 + 2Ph\cdot CO_2Na + 2H_2O$. An alcoholic solution of phenylhydrazine converts the dioxime into 1 : 2 : 3-*triketo*cyclo*hexanetriphenylhydrazone*, $C_{24}H_{24}N_6$, which crystallises in slender needles, m. p. 182—183°. The dioxime interacts with *o*-phenylenediamine, yielding

1-*oximino*-1 : 2 : 3 : 4-*tetrahydrophenazine*, $C_6H_4<\begin{matrix}N:C\cdot C(N\cdot OH)\cdot CH_2\\ N:C\text{---}CH_2\text{---}CH_2\end{matrix}$, small, glistening, brown crystals, m. p. 216—218°.

3 · 5-*Dioximino*-1-*methyl*-4-cyclo*hexanone*, $C_7H_{10}O_3N_2$, prepared from 4-methyl*cyclo*hexanone, crystallises in pale yellow leaflets, turns brown at 180°, and decomposes suddenly at 208°. The following derivatives are prepared by the methods just described: *dibenzoate*, small, pale yellow needles, decomposing at 172°; 3 : 4 : 5-*triketo*-1-*methyl*cyclo*hexanetriphenylhydrazone*, $C_{25}H_{26}N_6$, small, slender, yellow needles, m. p. 184°; 1-*oximino*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenazine*, $C_{13}H_{13}ON_3$, small, glistening, yellow needles, m. p. 210—211°. The parent substance is converted (1) by a cold solution of phenylhydrazine in glacial acetic acid into 3 : 5-*dioximino*-1-*methyl*cyclo*hexan*-4-*onephenylhydrazone*, $C_{13}H_{16}O_2N_4$, a crystalline, orange powder, m. p. 220° (decomp.); (2) an alcoholic solution of semicarbazide hydrochloride and sodium acetate into the *semicarbazone*, $C_8H_{13}O_3N_5$, which crystallises in spherical aggregates of small, colourless needles and decomposes at 200°; (3) by an alcoholic solution of hydroxylamine hydrochloride and sodium acetate into the corresponding *trioxime*, a colourless syrup, the *dibenzoate* (?) of which, $C_{21}H_{19}O_5N_3$, crystallises in small, colourless needles, m. p. 175°.

1 : 3-*Dioximino*-2-cyclo*pentanone*, $C_5H_6O_3N_2$, prepared from *cyclo*pentanone, crystallises in flat, yellow needles, and decomposes suddenly at 215°. W. H. G.

Catalytic Preparation of Aromatic Ketones. JEAN B. SENDERENS (*Compt. rend.*, 1910, **150**, 111—112. Compare Abstr., 1909, i, 286, 627; this vol., i, 11).—The following aromatic ketones are readily obtained by the method already described, namely: acetophenone, propiophenone, phenyl propyl ketone, phenyl *iso*propyl ketone, phenyl *iso*butyl ketone. To obtain a good yield, it is necessary to employ 3 mols. of the fatty acid to 1 mol. of benzoic acid, and to maintain the temperature of the catalyst at 380—460°. The product is always accompanied by smaller quantities of the symmetrical aliphatic ketone. Benzoic acid may be replaced by its anhydride. Benzophenone could not be obtained by this method. W. O. W.

Additive Compounds of Ketones and Quinones with Acids and Phenols. KURT H. MEYER (*Ber.*, 1910, **43**, 157—164. Compare Abstr., 1908, i, 731; 1909, i, 395).—Whereas acetophenone only forms colourless double salts with metallic chlorides, benzophenone in many cases yields light yellow compounds. A yellow *nitrate*, $C_{13}H_{10}O\cdot HNO_3$, has been isolated, whilst the faintly yellow-coloured solution of benzophenone in sulphuric acid undoubtedly contains a coloured sulphate. Benzophenone has, although to a much less extent, the same properties of halochromism as distyryl ketone. The coloured compounds of benzophenone could not be isolated, but those of fluorenone are more characteristic. Two series of double salts are formed, the one a deep violet, represented by the compound with aluminium bromide, and the other, orange in colour. The solution in

sulphuric acid apparently contains both forms, as the deep violet solution becomes orange-red on the gradual addition of water, and finally colourless when the fluorenone separates.

Fluorenone also combines with phenols, forming deeply-coloured products. With α-naphthol, two compounds are formed: an orange-yellow derivative from two molecules of fluorenone and one molecule of α-naphthol, and a red substance from one molecule of each component.

Similar compounds could not be obtained from distyryl ketone. Dianisylideneacetone, however, dissolves in phenol with an intense yellow coloration, and forms with α-naphthol a crystalline, orange-yellow compound, containing three molecules of α-naphthol to two molecules of the ketone.

These compounds of ketones and quinones with phenols are regarded as belonging to the same class of additive compounds as those with acids, metallic chlorides, and sulphur dioxide. Both classes possess a deep colour, pronounced crystallising power, and are easily resolved into their components by water, or when heated in solvents; their formation is exothermic. They are regarded as loose additive products to the quinonoid or ketone oxygen atom. *Fluorenone nitrate* forms orange-red needles; the *trichloroacetate* gives orange needles, m. p. 58°; the *mercurichloride*, $C_{13}H_8O,(HgCl_2)_2$, separates in lustrous, orange needles. The *stannichloride*, $(C_{13}H_8O)_2,SnCl_4$, forms brownish-yellow crystals. With sulphur dioxide a substance crystallising in orange needles is obtained, containing between 1 and $1\frac{1}{2}$ mols. of sulphur dioxide. *Fluorenone aluminium bromide* separates in dark red, almost black crystals. The *compound*, $2C_{13}H_8O,C_{10}H_8O$, produced on heating with α-naphthol, crystallises in long, orange needles, m. p. 66—67°. In presence of an excess of α-naphthol this is converted into $C_{13}H_8O,C_{10}H_8O$, separating in stout, red crystals, m. p. 89°.

The compound of 2 mols. of dianisylylideneacetone and 3 mols. of α-naphthol separates in long, orange needles, m. p. 69°. Dianisylylideneacetone and sulphur dioxide form an orange-yellow solution, giving rise to orange-yellow needles when concentrated.

Phenanthraquinone trichloroacetate, $C_{14}H_8O_2,C_2HO_2Cl_3$, crystallises in sealing-wax red needles, m. p. 138°. E. F. A.

Occurrence of β-Pinene and l-Pinocamphone in Hyssop Oil, and Some Observations on Isomerides in the Pinene Series. EDUARD GILDEMEISTER and HUGO KOHLER (*Festschrift Otto Wallach*, 1909, 414—438).—An account of part of this investigation has appeared previously (compare Schimmel & Co., Abstr., 1908, i, 666). l-Pinocamphone, obtained directly from hyssop oil, has b. p. 212—213°/752 mm., D_{15}^{15} 0·9662, n_D^{20} 1·47421, α_D $-13·7°$, whilst a sample prepared by reducing the dibromide had b. p. 212·5—213·5°/749 mm., D_{15}^{15} 0·9679, n_D^{15} 1·47509, n_D^{20} 1·47343, α_D $-19·33°$; the dibromide has $[\alpha]_D^{21}$ $-49·24°$ in ether; the *semicarbazone* has m. p. 228—229°; a small quantity of a second *semicarbazone*, m. p. about 182—183°, was also obtained; the *oxime* is a colourless oil, b. p. 105—110°/4 mm., which deposits well-defined crystals, m. p. about

37—38°, when kept for some time. The ketone is reduced by alcohol and sodium, yielding l-*pinocampheol*, long, matted needles, m. p. 67—68°, b. p. 217—218°, a_D −44·63°, $[a]_D^{21}$ −55·33° in alcohol, D_{15}^{15} 0·9678, n_D^{15} 1·48420, n_D^{20} 1·48335; the corresponding *phenylurethane* crystallises in silky needles, m. p. 76—77°. *l*-Pinonic acid, obtained by the oxidation of the ketone, is identical with that described by Barbier and Grignard (compare Abstr., 1908, i, 852); when acted on by concentrated sulphuric acid, it yields l-*menthoethylheptanonolide*, crystallising in rectangular plates, m. p. 46—47°.

An attempt to prepare a pure active pinene by way of the crystalline *xanthate*, m. p. 36—37°, derived from *l*-pinocampheol (compare Tschugaeff, Abstr., 1908, i, 93), led to the production of a mixture of pinene and a dicyclic *terpene*; the latter, when oxidised, gave a crystalline dicarboxylic *acid*, $C_{10}H_{16}O_4$, m. p. 192—193°.

W. H. G.

Constituents of Ethereal Oils. Tetrahydrosantalene, $C_{15}H_{28}$. FRIEDRICH W. SEMMLER (*Ber.*, 1910, **43**, 445—448. Compare Abstr., 1907, i, 431, 433, 1062; 1908, i, 433).—*Santalene dihydrochloride*, $C_{15}H_{24}$,2HCl, obtained by the addition of hydrogen chloride to santalene in methyl-alcoholic solution, has b. p. 140—142°/0·55 mm., D^{20} 1·076, and n_D 1·4976. When distilled under 10 mm. pressure, it decomposes to a certain extent, yielding hydrogen chloride, and, when boiled with alcoholic potassium hydroxide, yields β-santalene.

When the dihydrochloride is reduced with sodium and boiling ethyl alcohol, it yields a mixture of hydrocarbons boiling at 119—123°/9 mm. The unsaturated hydrocarbons may be removed from this mixture by treatment with ozone, when pure *tetrahydrosantalene*, $C_{15}H_{28}$, is obtained. It has b. p. 116—118°/9 mm., D^{20} 0·864, n_D 1·4676, and a_D +7°30′ (100 mm. tube). The hydrocarbon must be dicyclic, as it has all the properties of a saturated compound; it is thus analogous to dihydroeksantalol and dihydroeksantalic acid. J. J. S.

Action of Magnesium and Allyl Bromide on Menthone. P. RYSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1695—1698 Compare Javorsky, Abstr., 1909, i, 168).—1-*Methyl*-4-iso*propyl*-3-*allyl*-cyclo*hexan*-3-*ol*, $CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>C(CH_2\cdot CH{:}CH_2)\cdot OH$, obtained on decomposing by means of water the Grignard compound yielded by magnesium, allyl bromide, and menthone, is a mobile, colourless liquid, b. p. 130—131°/22 mm., D_4^{27} 0·9028, *n* 1·470035, with an odour like that of mint. On oxidation with permanganate, it yields (1) mentholacetic acid, $CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>C(CH_2\cdot CO_2H)\cdot OH$, which, when heated with potassium hydrogen sulphate, loses water and gives an acid, $C_{12}H_{20}O_2$; both of these acids were obtained by Wallach (Abstr., 1902, i, 799); (2) the *trihydric alcohol*,

$$CH_2<\begin{matrix}CHMe-CH_2\\CH_2\cdot CHPr^\beta\end{matrix}>C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

which is a pale yellow, syrupy, odourless liquid. T. H. P.

Behaviour of Alicyclic Hydroxylamines and Hydroxylamineoximes towards Nitrous Acid. I. GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 453—467. Compare Francesconi and Cusmano, Abstr., 1909, i, 723, 724).—*iso*Nitroamines form two classes of ethers: (1) NO·NR·OR′, which readily give up nitrous acid, and (2) $\underset{\underset{O}{\|}}{R\cdot N}{:}N\cdot OR$ or $\underbrace{R\cdot N-N}_{O}\cdot OR$, which, under similar conditions, are either stable or else yield nitrous oxide. Analogous behaviour is shown by the two classes of ether formed by the nitroamines, namely, (1) $NO_2\cdot NRR'$, which decompose, giving nitrous acid, and

$$(2)\quad R\cdot N{:}\underset{\underset{O}{\|}}{N}\cdot OR' \quad \text{or} \quad \underbrace{R\cdot N-N}_{O}\cdot OR' ,$$

which yield nitrous oxide. It seems, then, that in these ethers the complex $-N_2O_2-$ can be completely eliminated from the forms $-\underset{\underset{O}{\|}}{N}{:}N\cdot O-$, $N{:}\underset{\underset{O}{\|}}{N}\cdot O\cdot$, and $\underbrace{\cdot N-N}_{O}\cdot O\cdot$, but not from the forms $-N(NO_2)-$ and $-N(NO)\cdot O-$. Hence the nitroamines and *iso*nitroamines, which in the free state probably possess the forms $R\cdot NH\cdot NO_2$ and $R\cdot N(OH)\cdot NO$ respectively, retain these forms when they decompose with elimination of nitrous acid, but assume the forms $R\cdot N{:}NO\cdot OH$ and $R\cdot NO{:}N\cdot OH$ when decomposition is accompanied by separation of hyponitrous acid or nitrous oxide and water. As a rule, the known *iso*nitroamines exhibit one or other of the above two methods of decomposition, but the author finds that, by varying the conditions, pulegonenitrosohydroxylamine (mentho*iso*nitroamine) can be decomposed in both ways, and can hence react in the two forms:

$$CHMe<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot N(NO)\cdot OH \text{ and}$$

$$CHMe<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot NO{:}N\cdot OH.$$

By the action of hydroxylamine on pulegone, three compounds have been obtained: pulegonehydroxylamine, m. p. 154° (compare Beckmann and Pleissner, Abstr., 1891, 936), an oxime, m. p. 120° (compare Wallach, Abstr., 1896, i, 309), and [α] pulegonehydroxylamineoxime, m. p. 118° (compare Semmler, Abstr., 1905, i, 222). The author has obtained two new derivatives of pulegone, namely, an oxime, m. p. 98°, and a [β] hydroxylamineoxime, m. p. 143°. Wallach (Terpene und Campher, Leipzig, 1909) regards the oxime m. p. 120° as an oxime of *iso*pulegone, and the oxime m. p. 98° is either stereoisomeric with this,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2-\underset{\underset{N\cdot OH}{\|}}{C}\end{matrix}>C{:}CMe_2 \text{ and } CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2-\underset{\underset{OH\cdot N}{\|}}{C}\end{matrix}>C{:}CMe_2,$$

or structurally isomeric,

$$CHMe<\begin{matrix}CH_2-CH_2\\CH_2\cdot C(NOH)\end{matrix}>CH\cdot CMe{:}CH_2 \text{ and}$$

$$CHMe<\begin{matrix}CH_2-CH_2\\CH_2\cdot C(NOH)\end{matrix}>C{:}CMe_2.$$

The new hydroxylamineoxime, m. p. 143°, is stereoisomeric with that

described by Semmler (*loc. cit.*), such isomerism being due either to the oximic nitrogen, thus:

$$OH\cdot NH\cdot CMe_2\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ \underset{OH\cdot N}{\underset{\|}{C}}\text{——}CH_2\end{matrix}{>}CHMe \quad \text{and}$$

$$OH\cdot NH\cdot CMe_2\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ \underset{N\cdot OH}{\underset{\|}{C}}\text{——}CH_2\end{matrix}{>}CHMe$$

or to the method of rupture of the double linking of pulegone and the subsequent addition of hydroxylamine, thus:

$$\underset{Me}{\underset{|}{CH}}{<}\begin{matrix}CH_2\text{——}CH_2\\ CH_2\cdot C(NOH)\end{matrix}{>}CH\cdot\underset{NH\cdot OH}{\underset{|}{CMe_2}} \quad \text{and}$$

$$\underset{Me}{\underset{|}{CH}}{<}\begin{matrix}CH_2\text{——}CH_2\\ CH_2\cdot C(NOH)\end{matrix}{>}CH\cdot\overset{NH\cdot OH}{\overset{|}{CMe_2}}$$

Pulegoneoxime, $C_{10}H_{16}\colon NOH$, m. p. 98°, prepared by the action of hydrochloric acid on *iso*pulegoneoxime, m. p. 120°, forms groups of laminæ with triangular sections, reduces Fehling's solution, and is rapidly decomposed by heating with dilute sulphuric acid, but is not affected by boiling with alcoholic potassium hydroxide.

β-Pulegonehydroxylamineoxime, $C_{10}H_{20}O_2N_2$, which is obtained together with the α-isomeride and *iso*pulegoneoxime when pulegone and hydroxylamine react under certain conditions, forms shining needles, m. p. 143°, reduces Fehling's solution instantaneously in the cold, and, when dissolved in organic solvents, is oxidised by the air to nitroso-compounds of a blue colour.

Pulegonenitrosohydroxylamine,

$$CHMe{<}\begin{matrix}CH_2\text{—}CO\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CMe_2\cdot N(NO)\cdot OH,$$

prepared by the action of nitrous acid on pulegonehydroxylamine, forms irregular, hexagonal crystals, m. p. 35° (decomp.), gives Liebermann's and the diphenylamine reactions, and in ethereal or alcoholic solution gives a garnet-red coloration with ferric chloride; it does not reduce Fehling's solution, but forms a *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N\colon C_{10}H_{17}\cdot N(NO)\cdot OH$, m. p. 165° (decomp.), which gives Liebermann's and the diphenylamine reactions and a red coloration with ferric chloride. With hydroxylamine in alcoholic solution, pulegonenitrosohydroxylamine gives a white, hygroscopic *substance*, decomp. at 200°, which reduces Fehling's solution in the cold and gives Liebermann's reaction, but gives no coloration with ferric chloride. When suspended in water or dissolved in organic solvents, pulegonenitrosohydroxylamine is moderately stable, but in the dry state in the air, or in a vacuum, it undergoes rapid decomposition, yielding (1) pulegone and (2) 8-nitromenthone (compare Harries and Roeder, Abstr., 1900, i, 182), which results from the oxidation of the 8-nitrosomenthone formed initially by the action of the air and of the nitric acid eliminated. With nitrous acid, pulegonenitrosohydroxylamine gives

pulegone and nitro- and nitroso-menthones. The last two compounds are formed according to the equation :

$$C_{10}H_{17}O\cdot NH\cdot OH + C_{10}H_{17}O\cdot N(NO)\cdot OH + HNO_2 = C_{10}H_{17}O\cdot NO_2 + C_{10}H_{17}O\cdot N_2O + N_2 + 2H_2O.$$

The formation of pulegone by the action of nitrous acid is due to the diazotisation of the pulegonenitrosohydroxylamine, thus :

$$C_{10}H_{17}O\cdot N(NO)\cdot OH + HNO_2 = C_{10}H_{17}O\cdot N_2\cdot NO_3 + H_2O ;$$

the resulting aliphatic diazo-derivative is immediately decomposed by water into nitrogen, nitric acid, and 8-hydroxymenthone, the last compound then losing water and giving pulegone. When, however, decomposition of pulegonenitrosohydroxylamine occurs in presence of an alkali, it proceeds entirely in the one direction, the resultant products being pulegone and nitrous oxide: $C_{10}H_{17}O\cdot NO\colon N\cdot OH + H_2O = C_{10}H_{17}O\cdot OH + H_2O + N_2O$ and $C_{10}H_{17}O\cdot OH = C_{10}H_{16}O + H_2O$.

T. H. P.

New Occurrence of *l*-Camphor. THEODOR WHITTELSEY (*Festschrift Otto Wallach*, 1909, 668—670).—The oil obtained from a variety of "sage-brush" common to western North America, probably *Artemisia cana*, was found to have the following constants: D_{15}^{15} 0·9405 ; a_D^{19} $-19{\cdot}09°$; $n_D^{20\cdot5}$ 1·4702 ; acid number, 4·2, 4·1 ; ester number, 18·5, 19·8 ; saponification number, 22·7, 23·9 ; saponification number after acetylation, 111·8, 110·3. It contains *l*-camphor to the extent of at least 44·5%, an observation not without interest, for, with the exception observed by Wallach in the case of the broad-leafed *Salvia*, *l*-camphor has been found only in plants of the family *Compositae*.

W. H. G.

Coriander Oil. HEINRICH WALBAUM and WILHELM MÜLLER (*Festschrift Otto Wallach*, 1909, 654—667).—The sample of coriander oil examined had the following constants: D_{15}^{15} 0·8735 ; a_D $+10{\cdot}4°$; n_D^{20} 1·46387 ; acid number, 0 ; ester number, 20·22 ; ester number after acetylation, 159, corresponding with 49·65% of linalool ; it is possible to obtain, however, 70% of the latter substance by fractional distillation on a large scale. Roughly, 20% of the oil consists of almost equal quantities of *a*-*d*-pinene, *p*-cymene, and terpinenes (α- and γ-terpinene), together with very small quantities of β-pinene, dipentene, and possibly, also, phellandrene and terpinolene. The presence of decylaldehyde, geraniol, *l*-borneol, and esters of these alcohols was also established. In addition to the compounds mentioned, coriander oil contains small quantities of unknown substances, which are of importance in imparting aroma to the oil.

W. H. G.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1909, [ii], **10**, 19—43).—This contains the following new work:

[JUSTIN DUPONT and LOUIS LABAUNE.]—*Action of Hydrochloric Acid on Linalool and Geraniol* (compare Grosser, Abstr., 1882, 525 ; Barbier, *ibid.*, 1892, 1236 ; 1895, i, 78).—When dissolved in toluene and treated with gaseous hydrogen chloride at 100°, both alcohols yield *linalyl chloride*, $C_{10}H_{17}Cl$, D^{20} 0·9341, $[a]_D^{20}$ 1·50°, n_D^{20} 1·4813, and b. p. 95—96°/6 mm. This on treatment with silver nitrate in alcohol

regenerates linalool. The chloride obtained from geraniol could not be obtained quite pure. At $-4°$ to $+3°$ the action of hydrogen chloride on linalool or geraniol in toluene is more complicated. No water is formed until the mixture regains atmospheric temperature. The product formed is a mixture of linalyl chloride with a dichloro-derivative. Cinnamyl alcohol at 100° yields a *chloride*, C_9H_9Cl, D^{22} 1·0857, n_D^{22} 1·583, b. p. 115—116°/6 mm., which absorbs bromine, forming a *dibromide*, m. p. 104°, and on treatment with silver nitrate in alcohol yields a mixture of two alcohols, one of which may be phenylallyl alcohol (Klages and Klenk, Abstr., 1906, i, 638).

[J. LEROIDE.]—*Preparation of Fenchone free from Camphor.*—The best results were obtained by warming crude fenchone with aluminium chloride and then distilling under reduced pressure. For the detection of camphor the semicarbazide test was employed, which is sufficient to show the presence of 0·1% of camphor. By this means camphor was proved to occur naturally in fennel oil. Thujone cannot be eliminated from mixtures of this ketone with camphor and fenchone by treatment with aluminium chloride and bromine, and in such cases oxidation with nitric acid must be resorted to, the camphor being subsequently removed by treatment with aluminium chloride and bromine.

Four oils from the Comores Islands were examined, and gave the following results: Bigarade oil had D^{15} 0·8812, α_D +42°13′, and was insoluble in 80% alcohol.

Petitgrain oil had D^{15} 0·8650, α_D +42°18′, and saponification value 33·6.

Basil oil had D^{15} 0·9588, α_D 0°35′, and saponification value 4·2.

Citronella oil had D^{15} 0·8922, α_D −0°52′, aldehydes 80% (by bisulphite process), and was insoluble even in absolute alcohol.

Ylang-ylang oil, from Nossi-Bé, had D^{15} 0·9673, α_D −42°12′, acid value 1·4, saponification value 129·5, esters 45·3%, and total alcohols 42·7%.

Linaloe oil, from Cayenne, had D^{20} 0·8721, α_D −12°56′, n_D^{20} 1·4635, and contained methylheptenone, *d*-terpineol, geraniol, *l*-linalool, and nerol (?). T. A. H

Constituents of Oil of Lemon. EDUARD GILDEMEISTER and WILHELM MÜLLER (*Festschrift Otto Wallach*, 1909, 439—451).—Oil of lemon contains in addition to *l*-limonene a moderate quantity of *l*-β-pinene, and very small quantities of α-pinene, *i*-α-pinene, *l*-camphene, β-phellandrene, and γ-terpinene. The sesquiterpene obtained from the oil in small quantity (compare Burgess and Page, Trans., 1904, **85**, 414) is shown to be identical with bisabolene (compare Tucholka, Abstr., 1897, ii, 584); the same hydrocarbon is present in opoponax oil, oil of *Piper Volkensii* (compare Schmidt and Weilinger, Abstr., 1906, i, 299), and camphor oil.

The erythritol from γ-terpinene (compare Wallach, Abstr., 1908, i, 814) undergoes the following changes: (1) when boiled with acids it yields a mixture of thymol and carvacrol; (2) it yields a brominated *substance*, crystallising in large leaflets, m. p. 93—94°, when treated with an alkaline solution of hypobromite; (3) when oxidised with an

alkaline solution of potassium permanganate it yields oxalic acid and an acid, m. p. 147—149°, which is probably *iso*propyltartronic acid.

W. H. G.

Essential Oil from the Seeds of Monodora grandiflora. ROBERT LEIMBACH (*Festschrift Otto Wallach*, 1909, 502—512).—The oil obtained by the steam distillation of the seeds of *Monodora grandiflora* is a limpid, pale yellow oil, with an odour resembling cymene, D_{15}^{15} 0·8574, a_D^{15} $-46·25°$ in a 1-dcm. tube, acid number 3·9, saponification number 7—12. Nearly 90% of the oil consists of hydrocarbons, chiefly *l*-phellandrene, camphene, and *p*-cymene. The remainder, a heavy oil with an aromatic odour, contains palmitic acid, carvacrol, a *substance*, $C_{10}H_{16}O$, which reacts neither as an alcohol nor a ketone, a *sesquiterpene*, $C_{15}H_{24}$, b. p. 260—270°, D_{15}^{15} 0·9138, $a_D + 24°$, n_D^{16} 1·50513, a crystalline *substance*, m. p. 160—163°, and small quantities of other unknown substances.

W. H. G.

A Condensation Product of Coumaranone and its Conversion into Oxindirubin. KARL FRIES and W. PFAFFENDORFF (*Ber.*, 1910, **43**, 212—219).—The constitutions have been ascertained of the compound, $C_{18}H_{14}O_4$, obtained from 4-methyl-2-coumaranone or from ω-chloro-2-hydroxy-5-methylacetophenone (Abstr., 1909, i, 44), and also of those obtained by a similar process from 5-methyl-2-coumaranone or ω-chloro-2-hydroxy-4-methylacetophenone, and from 2-coumaranone or ω-chloro-2-hydroxyacetophenone. An ethereal solution of 2-coumaranone is treated with sodium and then with acetyl chloride, whereby the *acetate*, m. p. 106°, of 2-hydroxy-1 : 2′-dicoumarone, $C_6H_4<\begin{matrix}C(OH)\\O\end{matrix}>C\cdot C<\begin{matrix}C_6H_4\\CH\cdot O\end{matrix}$, is formed; the parent substance has not been obtained pure. By warming an alcoholic solution of the acetate with sodium ethoxide and subsequently acidifying, by boiling an acetic acid solution of the acetate with hydrogen peroxide, or by the prolonged heating of 2-coumaranone or ω-chloro-2-hydroxyacetophenone with alcoholic sodium ethoxide, 2 : 1′-*dihydroxy*-1 : 2′-*dicoumarone* (leuco-oxindirubin), $C_6H_4<\begin{matrix}C(OH)\\O\end{matrix}>C\cdot C<\begin{matrix}C_6H_4\\C(OH)\cdot O\end{matrix}$, m. p. 185°, is obtained, which forms orange-yellow needles, gives a deep red, non-fluorescent solution in concentrated sulphuric acid, and by the prolonged heating of its solution in glacial acetic acid, or, more readily, by treating the solution with hydrogen peroxide or bromine, is converted into "1 : 2-*biscoumaran-indigo*" (*oxindirubin*),

$$C_6H_4<\begin{matrix}CO\\O\end{matrix}>C:C<\begin{matrix}C_6H_4\\CO\cdot O\end{matrix},$$

m. p. 215°, which is also obtained by treating an acetic acid solution of 2-coumaranone and *o*-hydroxybenzoyl formic acid with concentrated sulphuric acid.

By a similar series of reactions, 5-methyl-2-coumaranone yields the *acetate*, m. p. 133°, of 2-hydroxy-5 : 5′-dimethyl-1 : 2′-dicoumarone, 2 : 1′-*dihydroxy*-5 : 5′-*dimethyl*-1 : 2′-*dicoumarone* (5 : 5′-*dimethyl-leuco-oxindirubin*), m. p. 204°, and "1 : 2′-*bis*(5-*methylcoumaran*)-*indigo*"

(5 : 5′-*dimethyloxindirubin*). The compound $C_{18}H_{14}O_4$ (*loc. cit.*) is 4 : 4′-dimethyl-leuco-oxindirubin. C. S.

Oxonium Perchlorates. KARL A. HOFMANN, A. METZLER, and H. LECHER (*Ber.*, 1910, **43**, 178—183. Compare Abstr., 1909, ii, 568).—Seventy per cent. perchloric acid yields crystalline compounds with ketones, and similar substances with basic properties; these are sparingly soluble and admirably adapted for characterising and isolating ketones. Even substances, such as carbazole, in which the basic properties of the nitrogen are very feeble, form crystalline salts. The perchlorates afford a better test of basic properties than picrates. These salts are regarded as oxonium derivatives.

A solution of xanthone in tetrachloroethane gives a bright yellow precipitate of *xanthone perchlorate*, $C_{13}H_8O_2,HClO_4$, which can be recrystallised from tetrachloroethane without decomposition, but is very rapidly decomposed by traces of moisture.

Carbazole perchlorate crystallises in lustrous, colourless plates; it is decomposed by water. Prolonged action with an excess of perchloric acid leads to the formation of a greenish-blue compound.

A colourless perchlorate is also formed by quinone di-imide. This explodes on heating. When moistened with water, it becomes a brilliant bluish-green, then violet, and then brown.

Benzophenone forms a yellow solution and a bright brownish-yellow, crystalline mass. This rapidly decomposes in moist air, leaving colourless oily drops, which do not crystallise until inoculated with a crystal of benzophenone. The perchlorate is apparently derived from the allotropic low melting variety of benzophenone.

Anthraquinone and alizarin do not react with perchloric acid. *Phenanthraquinone perchlorate* forms a mass of blood-red crystals in solution, which dry to red needles, but rapidly become bright orange when exposed to moist air. The *hemiperchlorate*, $(C_{14}H_8O_2)_2,HClO_4$, is obtained in flat, obliquely-cut, yellow or brownish-red prisms.

From retenequinone only the *hemiperchlorate* has been isolated. *Naphthazarin perchlorate* forms large, rectangular, stout plates with a bronze lustre. E. F. A.

New Selenium Compound. IDA FOA (*Gazzetta*, 1909, **39**, ii, 527—534).—*Selenophen*, $\begin{matrix}CH{:}CH\\ | \\ CH{:}CH\end{matrix}\!\!>\!Se$, obtained by heating sodium succinate with phosphorus triselenide, is a yellow, mobile, irritant liquid, b. p. 147—149°/250 mm.; it dissolves in concentrated sulphuric acid, giving a reddish-brown coloration, whilst with a solution of isatin in concentrated sulphuric acid, a dark carmine coloration is obtained. In presence of acetic acid, it forms with bromine an unstable, liquid bromide. T. H. P.

Production of a Volatile Aromatic Substance from Solutions of Morphine Salts. C. REICHARD (*Pharm. Zentr.-h.*, 1910, **51**, 128—130).—When a solution of morphine hydrochloride or sulphate in water is heated, a slight odour of musk is developed, and the

strength of this odour increases with the concentration of the alkaloidal solution, and with the quantity of water vapour produced from the solution. T. A. H.

Partial Racemism. H. DUTILH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 393—400).—The author has studied the partial racemism which occurs with strychnine racemate, more especially by observing the behaviour of this compound in presence of its aqueous solution. The investigation was carried out on the lines indicated by Roozeboom (Abstr., 1899, ii, 401), who pointed out the probable inaccuracy of the results obtained by Ladenburg and Doctor (Abstr., 1899, i, 310). By means of the solubility curves of the *d*-, *l*-, $l+r$-, and $d+r$-compounds at 40°, 25°, 16°, and 7·5°, it was found that the transition interval, which Ladenburg and Doctor assumed to be non-existent, extended over about 20°. Saturated solutions of the partial racemate are stable only below 7·5°, although the solubility at higher temperatures can be determined by retarding the decomposition.

The author has avoided determining by means of the polarimeter the content of the *l*- and *d*-compounds in liquids saturated with the $r+d$-, $r+l$-, or $d+l$-compounds, and suggests that such method of analysis gives a wrong idea concerning the inner composition of a solution saturated with two salts. This view is supported by the results obtained by Findlay and Hickmans (Trans., 1909, **95**, 1386), who, using the polarimetric method of estimation, found that the addition of *l*-menthyl *l*-mandelate diminishes the solubility of *l*-menthyl *d*-mandelate at 10°, whilst it increases it at 25° or 35°; such behaviour the author regards as improbable. T. H. P.

Hæmopyrrole. LEON MARCHLEWSKI (*Ber.*, 1910, **43**, 259—260).—Polemical. A reply to Piloty (this vol., i, 133). R. V. S.

Pyridine Hydrate. WILLIAM OECHSNER DE CONINCK (*Bull. Soc. chim. Belg.*, 1910, **24**, 55).—From basic tar oils the author has isolated a product which has the composition of a pyridine hydrate,

$$2C_5H_5N,7H_2O.$$

This has b. p. 91—93°, but it is not regarded as a definite chemical compound (compare Goldschmidt and Constam, Abstr., 1884, 611). T. A. H.

Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. VI. Tautomerism of Ethyl 2 : 6-Diphenyl-4-pyridone-3 : 5-dicarboxylate. PAVEL IW. PETRENKO-KRITSCHENKO and JOH. SCHÖTTLE (*Ber.*, 1910, **43**, 203—206).—The methylation of ethyl 2 : 6-diphenyl-4-pyridone-3 : 5-dicarboxylate in alkaline solution leads to the formation of 2 : 6-diphenyl-1-methyl-4-pyridone-3 : 5-dicarboxylic acid, m. p. 270°, and a mixture, m. p. 125—130° (Abstr., 1909, i, 605). By hydrolysing the latter by 7% aqueous alkali and subsequent acidification, an *acid*, $C_{20}H_{15}O_5N$, is obtained, which separates from dilute acetic acid in crystals, m. p. 240° (decomp.), containing $1\frac{1}{2}C_2H_4O_2$, and forms an *ethyl* ester, m. p. 229—230°, which is insoluble in ammonium

hydroxide. The acid is probably 4-methoxy-2 : 6-diphenylpyridine 3 : 5-dicarboxylic acid. C. S.

Anthranil. XVI. Relation of Anthroxanic Acid (2-Anthranilcarboxylic Acid) to Anthranil. EUGEN BAMBERGER and SVEN LINDBERG (*Ber.*, 1910, **43**, 122—127. Compare Abstr., 1909, i, 509, 510, 511).—*o*-Amino- and *o*-nitro-aromatic aldehydes and ketones are converted by mild oxidising and reducing agents respectively into anthranil derivatives. To establish the constitution of anthroxanic acid as anthranil-2-carboxylic acid, $C_6H_4<\begin{matrix}N\text{———}\\ \mid \\ C(CO_2H)\end{matrix}>O$, the behaviour of isatinic acid and *o*-nitrophenylglyoxylic acid has been studied.

By the oxidation of isatinic acid with Caro's reagent, anthroxanic acid, 2 : 2′-azoxybenzoic acid, and *o*-nitrosobenzoic acid are formed. The last product affords strong support to the view that *o*-hydroxylaminophenylglyoxylic acid, $OH{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, is the first intermediate oxidation product.

o-Nitrophenylglyoxylic acid, when reduced by tin and acetic acid, forms anthroxanic acid and a compound, m. p. 127°, probably 1-acetyldioxindole, $C_6H_4<\begin{matrix}CH(OH)\text{—}\\ N(CO{\cdot}CH_3)\end{matrix}>CO$. E. F. A.

Cinchonic Acid Syntheses. WALTHER BORSCHE (*Ber.*, 1910, **43**, 267).—A reply to Schiff (this vol., i, 134). R. V. S.

Elimination of Alkyl Radicles and Fission of Organic Bases by means of Cyanogen Bromide and Phosphorus Halides. JULIUS VON BRAUN (*Festschrift Otto Wallach*, 1909, 313—386).—A résumé of the author's investigations on this subject (compare Abstr., 1904, i, 688, 731, 841, 918; 1905, i, 596, 634, 636, 826; 1906, i, 576; 1907, i, 28, 79, 105, 110, 127, 151, 524, 728, 899, 960; 1908, i, 625, 627, 675, and 685). The following observations have not been recorded previously. Quinoline is converted by cyanogen bromide and water into a crystalline *substance*, m. p. 113°, which probably has the formula $C_6H_4<\begin{matrix}CH{=\!=}CH{\cdot}\\ N(CN){\cdot}CH{\cdot}OH\end{matrix}$.

Benzoylhexahydrocarbazole and the 4-methyl compound (compare Borsche, Abstr., 1908, i, 365), when acted on by phosphorus chlorides, yield 2-*benzoylaminodiphenyl*, m. p. 102°, and 2′-*benzoylamino*-4-*methyldiphenyl*, m. p. 121°, respectively. W. H. G.

Indigoid Dyes. V. Indigoid Dyes of the Anthracene Series. A. BEZDZIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1909, **30**, 871—878. Compare Abstr., 1909, i, 415, 417).—Isatin chloride and isatinanilide condense with hydroxy-derivatives of anthracene, forming indigoid dyes, which are far more stable towards acids and alkalis than the analogous naphthalene compounds (compare Abstr., 1908, i, 673); for example, 1-keto-2-indoxylanthracene is not decomposed by sodium hydroxide, although the isomeride, 2-keto-1-indoxylanthracene, when similarly treated yields anthranilic acid and 2-hydroxy-

1-anthracenealdehyde. The latter substance has the property of dyeing animal fibres and the skin an intense yellow:

$$\text{(I.)}\ \begin{matrix} C_{10}H_6\cdot CO \\ | \\ CH{=}CH \end{matrix}\!\!>C{:}C<\!\!\begin{matrix} CO \\ NH \end{matrix}\!\!>C_6H_4 \quad \text{(II.)}\ \begin{matrix} CH{-\!\!-}CO \\ \| \\ CH\cdot C_{10}H_6 \end{matrix}\!\!>C{:}C<\!\!\begin{matrix} CO \\ NH \end{matrix}\!\!>C_6H_4$$

1-*Keto*-2-*indoxylanthracene* (I), prepared by the condensation of α-anthrol and isatinanilide in acetic anhydride, crystallises in small, dark blue needles with a bronzy reflex, melts and sublimes with decomposition at a high temperature, and, when reduced with an alkaline solution of hyposulphite, yields an orange-red solution which dyes textile fibres a pure blue.

2-*Keto*-1-*indoxylanthracene* (II), similarly prepared from β-anthrol, forms small, dark blue needles with a coppery reflex, and sublimes with decomposition at a high temperature. 2-*Hydroxy*-1-*anthracenealdehyde*, $C_{15}H_{10}O_2$, crystallises in long, pale yellow needles, m. p. 164°; the *oxime* crystallises in four-sided, pale green plates, m. p. 197° (decomp.); the *phenylhydrazone* forms flat, yellow prisms, m. p. 224—225°; the *aldazine* forms slender, brick-red needles, m. p. above 300°.

5-*Hydroxy*-1-*keto*-2-*indoxylanthracene*, $C_{22}H_{13}O_3N$, prepared from 1:5-dihydroxyanthracene and isatin chloride, crystallises in long, slender, dark blue needles; the isomeric 8-*hydroxy*-compound is very similar in properties, but is slightly more green. W. H. G.

Synthesis of Oxazoles and Thiazoles. I. SIEGMUND GABRIEL (*Ber.*, 1910, **43**, 134—138).—By the action of phosphorus pentachloride on benzoylaminoacetophenone, 4-*chloro*-2:5-*diphenyloxazole* is formed, and not a chlorinated *iso*quinoline derivative, as might be expected from analogy to the synthesis of dihydro*iso*quinolines from acyl derivatives of phenylethylamine.

ω-Benzoylaminoacetophenone is best prepared from ω-aminoacetophenone hydrochloride by the action of benzoyl chloride in acetic acid solution; it has m. p. 124° [Robinson, Trans., 1909, **95**, 2169, gives 123°]. When heated with two mols. of phosphorus pentachloride, first at the temperature of the water-bath and later to 170°, 4-*chloro*-2:5-*diphenyloxazole*, $O<\!\!\begin{matrix} CPh{:}CCl \\ CPh{:}N \end{matrix}$, is formed, crystallising in slender needles, m. p. 67—68°. When heated with sodium amalgam in alcoholic solution, 2:5-diphenyloxazole, $O<\!\!\begin{matrix} CPh{:}CH \\ CPh{:}N \end{matrix}$, is obtained (compare E. Fischer, Abstr., 1896, i, 262). The same compound may be obtained in one operation from benzoylaminoacetophenone when only one molecule of phosphorus pentachloride is used. Similarly, when benzoylaminoacetophenone and phosphorus pentasulphide are heated at 170°, 2:5-*diphenylthiazole*, $S<\!\!\begin{matrix} CPh{:}CH \\ CPh{:}N \end{matrix}$, is formed, crystallising in large, rhombic plates, m. p. 103—104°. E. F. A.

Action of Hydrazines on Thiocyanoacetic Acid and its Ethyl Ester. GUSTAV FRERICHS and PAUL FORSTER (*Annalen*, 1910, **371**, 227—257).—The nature of the interaction of thiocyanoacetic acid and phenylhydrazine as described by Harries and Klamt (Abstr.,

1900, i, 413) not being strictly analogous to that of thiocyanoacetic acid and aniline (compare Rizzo, Abstr., 1898, i, 659; Beckurts and Frerichs, Abstr., 1902, i, 763), it was deemed advisable to repeat the work of the first-named investigators, the outcome of which has been the direct negation of many of the statements of these authors.

When phenylhydrazine is added to a cold ethereal solution of thiocyanoacetic acid, a white, crystalline precipitate of *phenylhydrazine thiocarbimidoacetate*, $SCN\cdot CH_2\cdot CO_2H,NH_2\cdot NHPh$, m. p. 92—100°, is obtained, which, when kept for some time, or when boiled with alcohol, passes into *carbaminethioglycollphenylhydrazide*,

$$NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

colourless leaflets, m. p. 149°. The latter substance is more readily obtained by the interaction of phenylhydrazine, chloroacetic acid, and potassium thiocyanate in alcoholic solution; when heated at about 155° for an hour, it passes into *dithiodiglycollphenylhydrazide*,

$$S_2(CH_2\cdot CO\cdot NH\cdot NHPh)_2,$$

which crystallises in colourless, glistening leaflets, m. p. 174°, and is also formed by heating carbaminethioglycollphenylhydrazide with 10% aqueous ammonia and treating the solution subsequently with hydrogen peroxide.

When ethyl thiocyanoacetate is boiled with an alcoholic solution of phenylhydrazine, it yields ammonium cyanate, a viscid, oily *substance*, and 3-*anilinothiohydantoin*, $\begin{array}{l}CH_2\text{—}CO\\ |\\ S\cdot C(NH)\end{array}\!\!>N\cdot NHPh$, colourless crystals, m. p. 176°, which dissolve in concentrated sulphuric acid and aqueous potassium hydroxide, forming blue and violet solutions respectively; the substance just described is also formed by the action of phenylthiosemicarbazide on chloroacetic acid. The interaction of chloroacetylphenylsemicarbazide and potassium thiocyanate in alcoholic solution leads to the formation of *thiocarbimidoacetylphenylsemicarbazide*, $SCN\cdot CH_2\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, small, glistening crystals, m. p. 172—173°, which, when boiled with water, yields 2-*imino*-5-*keto*-4-*phenyltetrahydro*-1 : 3 : 4-*thiodiazine*, $S\!\!<\!\!\begin{array}{l}C(NH)\cdot NH\\ CH_2\text{——}CO\end{array}\!\!>\!NPh$, crystallising in pale yellow needles, m. p. 161—162°; the crystalline *salts* with the halogen acids, $C_9H_9ON_3S,HX$, were prepared.

Hydrazine hydrate and thiocyanoacetic acid combine, yielding *hydrazine thiocarbimidoacetate*, $SCN\cdot CH_2\cdot CO_2H,N_2H_4$, glistening leaflets, m. p. 87—90°, which undergoes intermolecular rearrangement when kept, passing probably into *carbaminethioglycollhydrazide*,

$$NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

m. p. about 125°, and, when boiled with water, yields a *substance*, which decomposes at 280—290°, and could not be obtained pure. The action of hydrazine hydrate on ethyl thiocyanoacetate leads to the formation of 3 : 3-*bisthiohydantoin*, $\begin{array}{l}CH_2\text{—}CO\\ |\\ S\cdot C(NH)\end{array}\!\!>N\cdot N\!\!<\!\!\begin{array}{l}CO\text{——}CH_2\\ \qquad\quad\ |\\ C(NH)\cdot S\end{array}$; the same substance is formed by the interaction of bisthiocarbamide (hydrazodicarboxythioamide) and chloroacetic acid; it decomposes without melting at a high temperature.

Carbaminethioglycollphenylhydrazide undergoes the following

changes: (1) when boiled with 10% aqueous ammonia and subsequently treated with hydrochloric acid, it yields *thioglycollphenylhydrazide*, NHPh·NH·CO·CH_2·SH, leaflets, m. p. 112—113°; (2) it is converted by alcoholic potassium hydroxide and methyl iodide under pressure at 100° into *methylthioglycollphenylhydrazide*, $C_9H_{12}ON_2S$, glistening leaflets, m. p. 104—105°; the corresponding *ethyl* compound, $C_{10}H_{14}ON_2S$, forms colourless leaflets, m. p. 84—85°; (3) when heated with alcoholic potassium hydroxide and chloroacetamide, it yields *thiodiglycollamidephenylhydrazide*,

NH_2·CO·CH_2·S·CH_2·CO·NH·NHPh,

colourless leaflets, m. p. 135—136°; (4) with alcoholic potassium hydroxide and ethyl chlorocarbonate it yields *carboxythioglycollphenylhydrazide*, CO_2H·S·CH_2·CO·NH·NHPh, m. p. 156—157°; the *potassium* salt has m. p. 212—213°.

The following substances are prepared by methods similar to those just described: *phenylmethylhydrazinethiocyanoacetate*, m. p. 65—68°; *carbaminethioglycollphenylmethylhydrazide*, $C_{10}H_{13}O_2N_3S$, m. p. 145—146°; *methylthioglycollphenylmethylhydrazide*, $C_{10}H_{14}ON_2S$, needles, m. p. 74—75°; *carbethoxythioglycollphenylmethylhydrazide*, $C_{12}H_{16}O_3N_2S$, colourless leaflets, m. p. 82—83°; *carbaminethioglycoll*-p-*tolylhydrazide*, $C_{10}H_{13}O_2N_3S$, m. p. 164—165°; *thioglycoll*-p-*tolylhydrazide*, $C_9H_{12}ON_2S$, m. p. 125—126°; *dithiodiglycoll*-p-*tolylhydrazide*, $C_{18}H_{22}O_2N_4S_2$, glistening leaflets, m. p. 182—183°; *methylthioglycoll*-p-*tolylhydrazide*, $C_{10}H_{14}ON_2S$, glistening leaflets, m. p. 108—109°; *thiodiglycollamide*-p-*tolylhydrazide*, $C_{11}H_{15}O_2N_3S$, glistening, pale yellow needles, m. p. 148—149°. W. H. G.

Case of Isomerism. [Acylazoaryl Compounds.] GIACOMO PONZIO (*Gazzetta*, 1909, **39**, ii, 535—546).—The author has carried out further investigations on the yellow, white, and red isomerides, $C_{13}H_{10}O_4N_4$, obtained by the action of benzenediazonium acetate on the potassium derivative of ω-dinitrotoluene (Abstr., 1908, i, 482, 582; 1909, i, 443, 681). The results obtained settle definitely the structure of the red isomeride, and render probable the accuracy of that already assigned to the white compound, but do not admit of the structure of the yellow derivative being determined.

For the yellow compound, the author has suggested the formula NO_2·CPh(NO)·O·N:NPh, which would explain its isomeric change into α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine (Abstr., 1908, i, 482). On the basis of this formula, Dimroth and Hartmann (Abstr., 1909, i, 66) indicate an analogy between this yellow compound and benzene-*O*-azotribenzoylmethane, obtained by the interaction of the potassium derivative of tribenzoylmethane with benzenediazonium acetate, and suggest that the yellow compound is a true *O*-azoderivative and not a diazo-derivative. But, apart from the fact that the properties of Dimroth and Hartmann's compound are explained equally well by regarding it as a true diazonium salt (compare Auwers, Abstr., 1909, i, 67), its analogy to the author's yellow compound is not borne out by its behaviour with ethereal hydrochloric acid. Thus, benzene-*O*-azotribenzoylmethane gives benzenediazonium chloride and tribenzoylmethane, whilst the diazobenzene

derivative of ω-dinitrotoluene gives the isomeric compounds, α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine and ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone, $NO_2 \cdot CPh:N \cdot NH \cdot C_6H_4 \cdot NO_2$, treatment with water converting the former of these isomerides into β-nitroso-α-benzoyl-β-phenylhydrazine and leaving the latter unchanged. The formula $NO_2 \cdot CPh(NO) \cdot N:NPh$ for the yellow compound (*vide supra*) does not, however, explain its reaction with alcohol, with formation of ω-dinitrotoluene, nitrogen, acetaldehyde, and benzene.

The reactions of the red isomeride are not in accord with the structure, $NPh:N \cdot CPh(NO_2)_2$, originally assigned to it (Abstr., 1908, i, 482). Thus, on reduction by means of tin and hydrochloric acid, it yields ammonia, benzoic acid, and *p*-phenylenediamine. By sodium methoxide it is converted into α-dinitrotetraphenyltetrazoline (compare Bamberger and Grob, Abstr., 1901, i, 296). These results indicate that the red compound is not ω-benzeneazo-ω-dinitrotoluene, but ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone (compare Bamberger and Grob, Abstr., 1901, i, 567), and direct comparison confirms this indication. The isomeric change of the yellow compound into ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone consists in the passage of a nitro-group from an aliphatic carbon atom into the para-position of the benzene nucleus, and such a transformation is best explained by regarding the yellow compound as ω-benzeneazo-ω-dinitrotoluene, $NPh:N \cdot CPh(NO_2)_2$.

It follows from these results that the compound, m. p. 130—135°, previously described as ω-dinitro-ω-benzeneazo-*p*-xylene, must be regarded as ω-nitro-*p*-tolualdehyde-*p*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N:C(NO_2) \cdot C_6H_4Me,$$

and that described as ω-dinitro-ω-benzeneazo-*p*-methoxytoluene, m. p. 141—148°, as ω-nitroanisaldehyde-*p*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N:C(NO_2) \cdot C_6H_4 \cdot OMe.$$

But, in addition to the diazobenzene derivatives of the primary dinitrohydrocarbons, the ortho-substituted diazo-salts are also transformed into red isomerides when dissolved in moist ether, and in this case, too, there takes place transference of a nitro-group from the aliphatic carbon atom to the para-position of the benzene nucleus. So that the compound, m. p. 137° (decomp.), previously described (Abstr., 1909, i, 443) as ω-*o*-tolueneazo-ω-dinitrotoluene must be regarded as ω-nitrobenzaldehyde-*p*-nitro-*o*-tolylhydrazone,

$$NO_2 \cdot C_6H_3Me \cdot NH \cdot N:CPh \cdot NO_2,$$

a structure which is confirmed by the fact that it yields benzoic acid, ammonia, and 2 : 5-diaminotoluene on reduction with tin and hydrochloric acid; this compound may also be obtained by the interaction of the sodium derivative of ω-nitrotoluene and *m*-nitro-*o*-toluenediazonium sulphate: $CHPh:NO_2Na + NO_2 \cdot C_6H_3Me \cdot N_2 \cdot HSO_4 = NaHSO_4 + NO_2 \cdot C_6H_3Me \cdot NH \cdot N:CPh \cdot NO_2$. Further, the compounds described as ω-*o*-chlorobenzeneazo-ω-dinitrotoluene, m. p. 140° (decomp.), and ω-*o*-bromobenzeneazo-ω-dinitrotoluene, m. p. 140° (decomp.) (Abstr., 1909, i, 443), must be regarded as the *o*-chloro-*p*-nitrophenylhydrazone and *o*-bromo-*p*-nitrophenylhydrazone respectively of ω-nitrobenzaldehyde, $NO_2 \cdot C_6H_3Cl \cdot NH \cdot N:CPh \cdot NO_2$ and

$$NO_2 \cdot C_6H_3Br \cdot NH \cdot N:CPh \cdot NO_2.$$

These results explain the observation that, whilst the ortho-substituted diazonium salts give with moist ether their red isomerides, that is, the corresponding ortho-substituted *p*-nitrohydrazones, para-substituted diazonium salts, under the same conditions, lose two atoms of nitrogen and three of oxygen in the form of nitrous compounds, giving acylazoaryl derivatives, the isomeric acylarylnitronitrosohydrazines being formed as intermediate products: $R \cdot C(N_2O_4) \cdot N_2Ar \longrightarrow R \cdot CO \cdot N(NO_2) \cdot NAr \cdot NO \longrightarrow R \cdot CO \cdot N{:}NAr$; the para-position which the nitro-group tends to assume is in these cases occupied. It is found, indeed, that these compounds, by the action of absolute alcohol in the cold, give small yields of red isomerides, the nitro-group entering the benzene nucleus in the ortho-position. The red isomeride, m. p. 153—154° (decomp.), of the *p*-diazotoluene derivative of ω-dinitrotoluene (Abstr., 1909, i, 443) is found to be, not ω-*p*-tolueneazo-ω-dinitrotoluene, but ω-nitrobenzaldehyde-*o*-nitro-*p*-tolylhydrazone, $NO_2 \cdot C_6H_3Me \cdot NH \cdot N{:}CPh \cdot NO_2$; reduction of this compound (which may also be obtained by the interaction of the sodium derivative of ω-nitrotoluene and *m*-nitro-*p*-toluenediazonium sulphate: $CHPh{:}NO_2Na + NO_2 \cdot C_6H_3Me \cdot N_2 \cdot HSO_4 = NaHSO_4 + NO_2 \cdot C_6H_3Me \cdot NH \cdot N{:}CPh \cdot NO_2$) with tin and hydrochloric acid gives benzoic acid, ammonia, and 3 : 4-diaminotoluene. Similarly, the compound described as ω-*p*-chlorobenzeneazo-ω-dinitrotoluene (Abstr., 1909, i, 443), m. p. 161° (decomp.), must be regarded as ω-nitrobenzaldehyde-*p*-chloro-*o*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_3Cl \cdot NH \cdot N{:}CPh \cdot NO_2,$$

and that described as ω-*p*-bromobenzeneazo-ω-dinitrotoluene as ω-nitrobenzaldehyde-*p*-bromo-*o*-nitrophenylhydrazone,

$$NO_2 \cdot C_6H_3Br \cdot NH \cdot N{:}CPh \cdot NO_2.$$

That the white isomeride, best obtained by dissolving the diazobenzene derivative of ω-dinitrotoluene in anhydrous benzene, is α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine, $NO_2 \cdot NBz \cdot NPh \cdot NO$, is confirmed by its transformation into benzoylazobenzene, $NBz{:}NPh$ (Abstr., 1909, i, 681). T. H. P.

Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1909, **39**, ii, 546—556).—The action of the sodium derivative of ω-*iso*nitrophenylacetonitrile on benzenediazonium acetate yields benzeneazo-ω-nitrophenylacetonitrile, $NO_2 \cdot CPh(CN) \cdot N{:}NPh$, which, by the passage of the nitro-group to the para-position of the benzene nucleus, undergoes spontaneous transformation into ω-cyanobenzaldehyde-*p*-nitrophenylhydrazone, $CN \cdot CPh{:}N_2H \cdot C_6H_4 \cdot NO_2$, and a small proportion of the corresponding *o*-nitrophenylhydrazone. This transformation, which is similar to that observed with the diazobenzene derivative of ω-dinitrotoluene (compare preceding abstract), also takes place with substituted diazo-derivatives, the nitro-group entering the benzene nucleus in the ortho-position in cases where the para-position is occupied. The initial compounds formed from ω-nitrophenylacetonitrile are, however, less stable than those yielded by ω-dinitrotoluene, and undergo isomeric change so rapidly that they

cannot be obtained in the dry state. Still more unstable are the compounds formed by ω-nitrotoluene with diazonium-salts, this reaction always giving ω-nitrobenzaldehydephenylhydrazones. In the latter case, it is a hydrogen atom from the aliphatic carbon atom which converts the group $\cdot N\colon N\cdot$ into $\colon N\cdot NH\cdot$, whilst in the previous cases it is the hydrogen atom from the para- (or ortho-) position of the benzene nucleus.

Benzeneazo-ω-nitrophenylacetonitrile, $NO_2\cdot CPh(CN)\cdot N\colon NPh$, forms a pale yellow, flocculent precipitate.

ω-Cyanobenzaldehyde-p-*nitrophenylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

crystallises in yellow plates, m. p. 208—209°, dissolves in alkali hydroxides, forming intensely violet solutions, and, on reduction by means of tin and hydrochloric acid, yields benzoic and hydrocyanic acids and *p*-phenylenediamine.

ω-Cyanobenzaldehyde-o-*nitrophenylhydrazone*, $C_{10}H_{14}O_2N_4$, crystallises in orange-red, flattened needles, m. p. 187°, gives a reddish-brown coloration when dissolved in alkali hydroxide solution, and yields benzoic and hydrocyanic acids and *o*-phenylenediamine when reduced with tin and hydrochloric acid.

ω-Cyanobenzaldehyde-p-*nitro*-o-*tolylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

obtained by the isomeric change of *o*-tolueneazo-ω-nitrophenylacetonitrile (prepared by the interaction of the sodium derivative of *iso*nitrophenylacetonitrile and *o*-toluenediazonium acetate), crystallises from benzene in brownish-yellow needles, m. p. 188°, forms intensely violet solutions with alkali hydroxide, and yields benzoic and hydrocyanic acids and 2 : 5-tolylenediamine on reduction.

ω-Cyanobenzaldehyde-o-*nitro*-p-*tolylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

formed by the isomeric transformation of *p*-tolueneazonitrophenylacetonitrile, crystallises in orange-red needles, m. p. 160°, gives a wine-red coloration with alkali hydroxides, and yields benzoic and hydrocyanic acids and 3 : 4-tolylenediamine on reduction.

ω-Cyanobenzaldehyde-o *chloro*-p-*nitrophenylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_3Cl\cdot NO_2,$$

prepared from *o*-chlorobenzenediazonium acetate and the sodium derivative of ω-*iso*nitrophenylacetonitrile, forms orange-coloured needles, m. p. 182°, and gives violet-red solutions with alkali hydroxides.

ω-Cyanobenzaldehyde-p-*chloro*-o-*nitrophenylhydrazone*, formed from *p*-chlorobenzeneazonitrophenylacetonitrile by isomeric change, crystallises in brownish-yellow laminæ, m. p. 240°, and gives intensely violet solutions with alkali hydroxides in presence of a small quantity of alcohol.

ω-Cyanobenzaldehyde-o : p-*dinitrophenylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_3(NO_2)_2,$$

formed by isomeric change of either *o*- or *p*-nitrobenzeneazonitrophenylacetonitrile, crystallises in reddish-brown prisms, m. p. 246° (decomp.), and gives intensely violet solutions with alkali hydroxide in presence of a drop of alcohol. T. H. P.

Limiting Cases between Polymorphism and Isomerism. ROBERTO CIUSA and MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 621—626).—*m*-Nitrobenzaldehydephenylmethylhydrazone forms two modifications, one red and the other yellow, both having m. p. 120—125° (Labhardt and Zembruski, Abstr., 1900, i, 125, found 112°, and Bamberger and Pemsel, Abstr., 1903, i, 286, 112—113°), at which temperature mixtures of the two also melt. The yellow form has the normal molecular weight in freezing benzene, the solution depositing the red modification on evaporation. Certain solvents, such as chloroform and benzene, convert the yellow into the red form, which may also be obtained by strongly cooling solutions of the yellow modification, or by seeding an alcoholic solution of either form with the red crystals. The red modification passes into the yellow on boiling with alcohol or ethyl acetate, on seeding its alcoholic solution with a yellow crystal, or on prolonged immersion in water or alcohol. There is no apparent or spectroscopic difference between solutions of the two products even when these are freshly dissolved. Both forms give with picryl chloride one and the same additive compound, which undergoes a considerable amount of dissociation even in concentrated alcoholic solution, giving the red hydrazone.

p-Nitrobenzaldehydephenylmethylhydrazone also occurs in two forms, one red and the other yellow, both having m. p. 130° (Labhardt and Zembruski, *loc. cit.*, found 132°). In this case, too, each form can be transformed into the other, but the change in colour is less distinct than with the meta-isomeride, and the red modification is very unstable unless stored under special conditions. *o*-Nitrobenzaldehydephenylmethylhydrazone occurs only in a red form, m. p. 90° (Labhardt and Zembruski, *loc. cit.*, found 77°), but *m*-nitroanisaldehyde-*p*-nitrophenylhydrazone, which is yellow when perfectly dry, becomes red immediately in moist air (Abstr., 1907, i, 137).

The criteria given by Wegscheider (Abstr., 1902, ii, 126) are insufficient to indicate whether this phenomenon is a case of isomerism or one of polymorphism. In this and in other cases, the phenomena of polymorphism and of isomerism approach so closely that the existence of a line of demarcation is not evident (compare Fock, this vol., ii, 23). T. H. P.

Pantachromism of Dimethyl- and Diphenyl-violurates. ARTHUR HANTZSCH and ROBERT ROBISON (*Ber.*, 1910, **43**, 45—68. Compare Abstr., 1909, i, 331, 333, 335).—In addition to the yellow lithium dimethylviolurate (*loc. cit.*, i, 335), a *red* salt, $C_6H_6O_4N_3Li$, has been prepared. It yields carmine-red compounds with 1EtOH and $1H_2O$. The yellow salt becomes red in the presence of traces of water. The solutions of the two lithium salts in pyridine are red, and in phenol, orange-coloured. A yellow compound with phenol, $C_6H_6O_4N_3Li,PhOH$, is described; it loses phenol when exposed to the air, and forms the red hydrated salt.

When the violet sodium salt is exposed to the air, it absorbs moisture (1 mol.) and becomes red. A *red* anhydrous sodium salt can be prepared by heating the compound containing ethyl alcohol. The

compound with phenol (1PhOH) is yellow, and when heated at 100° with methyl alcohol yields the anhydrous red salt. The blue potassium salt when exposed to the atmosphere yields the violet hydrate ($\frac{1}{2}H_2O$); the corresponding *phenol* compound has a rose-red colour.

The bluish-violet rubidium salt (*loc. cit.*, 334) contains $0·5H_2O$, and when boiled with methyl alcohol yields a pure *blue* anhydrous salt; the *phenol* compound has a rose-red colour. The *caesium* salt crystallises from alcohol in deep indigo-blue needles, and yields a rose-red phenoxide. Dimethylvioluric acid and phenol yield a yellow additive compound. Two coloured *silver pyridine* salts, $C_6H_6O_4N_3Ag,C_5NH_5$, have been prepared: a labile *green* salt by the addition of ether to the pyridine solution of brown silver dimethylviolurate, and a stable *bluish-violet* salt obtained when the green salt is left in contact with ether and pyridine.

The *methylamine* salt, $C_6H_7O_4N_3,NH_2Me$, has a rose-red colour, and when exposed to the air yields the yellow acid salt; the *dimethylamine* salt is violet, the *normal trimethylamine* salt is blue, the *acid* salt orange-yellow, and the *tetramethylammonium* salt is blue. The ethylamine salts are very similar. The normal tripropylamine salt could not be isolated; the *acid* salt, $2C_6H_7O_4N_3,NPr_3$, is orange-yellow. The *dibenzylamine* salt exists in a labile red and a stable bluish-violet modification. *Piperidine* yields a stable blue and a labile red salt, $C_6H_7O_4N_3,C_5H_{11}N$. *Pyridine* yields a stable yellow acid salt.

Diphenylvioluric acid was prepared by a modification of Whiteley's method (Trans., 1907, 91, 1330); the pure neutral salts are best prepared in alcoholic solution, as they readily decompose in the presence of aqueous alkalis. They crystallise with alcohol, which can be completely removed by heating the very finely divided salt. The *lithium* and *sodium* salts exist in labile red and stable yellow modifications, and yield red compounds with 1EtOH. The *ammonium* salt forms a violet compound with EtOH. The *normal potassium, rubidium,* and *caesium* salts are blue, and the *acid rubidium* and *caesium* salts green; the *magnesium* and *zinc* salts are yellow; the *thallous silver* salts exist in stable green and labile colourless forms. The *acid silver* salt, $C_{32}H_{21}O_8N_6Ag,3H_2O$, has an orange colour. The salts of dimethyl- and diphenyl-violuric acids exhibit both pantachromism and chromotropism. The labile forms of the salts are usually stable when perfectly dry, but pass readily into the more stable forms in the presence of a little water or alcohol. An increase in the depth of colour of the salts is observed as the metallic radicle becomes more positive, and in the case of substituted ammonium salts an increase in depth of colour is observed with an increase in the number of alkyl groups. The addition of phenol to the molecule of the alkali salts results in a diminution of colour, whereas the addition of pyridine produces an increase in colour, except in the case of the compound of silver violurate and pyridine, which is colourless, and to which the formula

$$CO{<}{\substack{N:C(OPy)\\N:C(OPy)}}{>}C:N\cdot OAg$$

is ascribed.

An increase in the depth of colour with an increase in the positive

nature of the metallic radicle is noticed in the case of concentrated aqueous or alcoholic solutions, and also of solutions in non-ionising solvents, such as chloroform or phenol. A negative solvent tends to lessen the depth of colour of the solution of any given salt. Molecular-weight determinations in phenol and ethyl acetate indicate that the different coloured isomeric salts are unimolecular.

The absorption spectra solutions of the acids and of their alkali salts have been measured.

A comparison of the absorption curves for diphenylvioluric acid, its lithium and cæsium salts, and nitroso*iso*propylacetone (Baly and Desch) points to the conclusion that the blue violurates should be represented as nitroso-enolic salts: $CO<\begin{matrix}NR\cdot CO\text{———}\\NR\cdot(COMe)\end{matrix}>C\cdot NO$.

The violuric acids as true oximino-ketones are the more completely transformed into the structurally isomeric nitroso-enols the more positive the nature of the metallic radicle present and the solvent.

J. J. S.

Pantachromic Salts of Oximino-oxazolones. ARTHUR HANTZSCH and J. HEILBRON (*Ber.*, 1910, **43**, 68—82. Compare Hantzsch and Kemmerich, Abstr., 1909, i, 336).—*p*-Bromo- and *p*-methoxy-derivatives of oximinophenyloxazolone yield pantachromic salts with colourless bases. The esters and acyl derivatives on the other hand are only pale yellow. The salts of the bromo-derivative are comparatively stable, and dissolve in various neutral solvents. Molecular-weight estimations in acetone, pyridine, and chloroform indicate that the salts, both ammonium and metallic, are unimolecular in solution. The colours of the salt solutions in non-ionising media increase in depth with the positive nature of the metallic radicle present.

The absorption spectra, both visible and ultra-violet, of the oxazolones and their salts in different solvents have been tabulated. The free acids are true oximino-compounds, and their absorption spectra resemble those of their ethers and acyl derivatives. The phenolic solution of the oximino-compound is distinctly yellow. The ultra-violet spectra of the salts do not differ materially from those of the free acids, but the visible spectra of the salts show characteristic absorption bands which are not present in the spectra of the free acids. The blue solutions of the potassium, rubidium, cæsium, and tetra-alkylammonium salts give practically identical spectra. The conclusion is drawn that the yellow salts derived from feeble bases possess the true oximino-ketone structure, whereas the blue salts derived from strong bases have a nitroso-enolic structure.

p-*Bromophenyloxazolone*, prepared from ethyl *p*-bromobenzoylacetate and hydroxylamine, crystallises in glistening plates, m. p. 118° (decomp.), and reacts with nitrous acid, yielding *oximino*-p-*bromophenyloxazolone*, $C_6H_4Br\cdot C<\begin{matrix}N\text{————}O\\C(:N\cdot OH)\cdot CO\end{matrix}$, which crystallises as a pale yellow monohydrate. The anhydrous compound has a pure

yellow colour and decomposes at 166°. The salts readily decompose in aqueous alkaline solutions, but are stable in alcoholic solution. The *lithium* salt, $C_9H_4O_3N_2BrLi$, exists in a stable yellow form only; the *sodium* salt forms orange-red needles, which form a pale rose-coloured *monohydrate*. The *potassium* salt exists in a rose-red and a reddish-violet form, and forms a pale red *phenol* compound, $C_9H_4O_3N_2BrK,C_6H_5{\cdot}OH$. The *acid potassium* salt is yellow. Rose, blue, and violet *rubidium* salts have been prepared; the *acid* salt is golden-yellow, and the *phenol* compound, pale red. Rose-coloured and bluish-violet *caesium* salts, together with pale red *phenol* compound, are described. The *barium* salt, $(C_9H_4O_3N_2Br)_2Ba,4H_2O$, is red, but when dehydrated is orange-coloured. Similar *calcium* and *magnesium* salts have been obtained. The *zinc* salt, $(C_9H_4O_3N_2Br)_2Zn$, is pale yellow, the *lead* salt pale rose, and the *thallium* salt flesh-coloured. A *blue*, an *orange*, and a *flesh-coloured silver* salt have been prepared, and a carmine-red monohydrate; the orange and the blue salts yield the same methyl ether. The silver salts are insoluble in neutral media, but dissolve in pyridine, yielding dichromatic solutions. The following additive compounds are described: $C_9H_4O_3N_2BrAg,2C_5H_5N$, violet; $C_9H_4O_3N_2BrAg,2NH_3$, deep blue; $C_6H_4O_3N_2BrAg,NH_3$, rose; $C_9H_4O_3N_2BrAg,CH_3CN$, carmine-red.

The *ammonium* salt is orange-coloured; the *methylamine*, *ethylamine*, *propylamine*, and *benzylamine* salts are rose-coloured; the *dimethylamine* and *diethylamine* salts are salmon-red; the *dipropylamine* salt, orange-coloured; the *dibenzylamine* salt, red; the *trimethylamine* salt, violet; the *triethylamine* salt, bluish-violet; the *tripropylamine* salt is red, and the *quaternary ammonium* salts crystallise in deep blue plates and their solutions resemble those of the alkali salts. The normal *pyridine* and *picoline* salts are pale yellow. The *methyl ether*,

$$C_6H_4Br{\cdot}C{<}\begin{matrix}C(:N{\cdot}OMe){\cdot}CO\\ N\text{———————}O\end{matrix},$$

forms pale yellow crystals, m. p. 129° (decomp.). The *acetyl* derivative also forms yellow crystals, m. p. 161° (decomp.), and the *benzoyl* derivative decomposes at 167°.

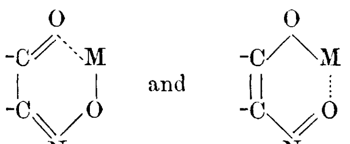
Anisyloxazolone, $OMe{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}CH_2{\cdot}CO\\ N\text{——}O\end{matrix}$, forms crystals with a satiny lustre, and m. p. 140—141° (decomp.). The *oximino*-derivative, $OMe{\cdot}C_6H_4{<}\begin{matrix}C(:NOH){\cdot}CO\\ N\text{———————}O\end{matrix}$, forms a yellow *monohydrate*; the anhydrous compound has a deeper yellow colour, and decomposes at 149°. The salts are not so polychromatic as those of the corresponding bromine derivatives

The following salts are described: *Sodium*, $C_{10}H_7O_4N_2Na$, orange-red; *potassium*, reddish-purple needles; *caesium*, bluish-violet; *ammonium*, red; *silver*, labile rose-coloured and stable blue; $C_{10}H_7O_4N_2Ag,2NH_3$, red. The *methyl ether*, $C_{11}H_{10}O_4N_2$, crystallises in pale yellow needles, m. p. 126°, and when hydrolysed yields *anisylfurazancarboxylic acid*, $OMe{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}C(CO_2H):N\\ N\text{———————}O\end{matrix}$, m. p. 99—100°. This acid is undoubtedly formed by the addition of water

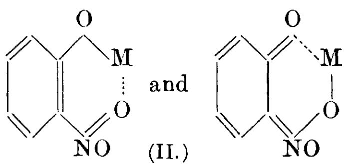
and the opening of the oxazolone ring, and the subsequent elimination of methyl alcohol. J. J. S.

Pantachromism of Violurates and Salts of Analogous Oximino-ketones. ARTHUR HANTZSCH (*Ber.*, 1910, 43, 82—91).—The following general conclusions are given: (1) all polychromatic salts are unimolecular in solution, pointing to the isomerism and not polymerism of different coloured salts derived from the same metal; (2) the solutions pass from yellow or orange through red and violet to blue as the positive nature of the metallic radicle increases; (3) the absorption curves of yellow solutions are somewhat analogous to the curves for solutions of the free oximino-ketones in indifferent solvents and to solutions of their acyl and methyl derivatives. Deep blue solutions, on the other hand, show distinct selective absorption, and are optically closely related to blue aliphatic nitroso-compounds. The change in colour is attributed to a chemical change, namely, to the passage from the oximino-ketone form to the nitroso-enolic form: $O{:}C{\cdot}C{:}N{\cdot}OH \longrightarrow OH{\cdot}C{:}C{\cdot}NO$.

All solutions of the salts consist of an equilibrated mixture of the two forms, the proportions of each depending on the positive character of the metallic or substituted ammonium radicle present, and also on the nature of the solvent. It is shown that a mixture of the yellow acetone solution of zinc diphenylviolurate with the blue acetone solution of potassium diphenylviolurate is red and not green.



(I.)



(II.)

Leuco-salts yield yellow solutions, indicating a partial conversion into the nitroso-enolic form. The solid salts of orange, red, or purple colour are also regarded as mixed crystals of the two isomeric salts.

When a salt exists in a yellow and a blue form, these are regarded as isomeric in the sense of Werner's valency-isomerism (for example, I).

Similarly, the yellow and red salts of nitrophenol are represented as (II)

The red *aci*-ethers are regarded as analogous to the red salts. J. J. S.

Purpuric Acid. ARTHUR HANTZSCH and ROBERT ROBISON (*Ber.*, 1910, 43, 92—95).—The formula of Piloty and Slimmer and Stieglitz (Abstr., 1904, i, 634) for purpuric acid is analogous to that of the blue violurates: $CO\left<\begin{matrix}NH\text{——}CO\\NH\cdot C(OH)\end{matrix}\right>C\cdot NO$ and $CO\left<\begin{matrix}NH\text{——}CO\\NH\cdot C(OH)\end{matrix}\right>C\cdot N{:}C\left<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right>CO$.

It has not been found possible to prepare coloured ethers or to isolate the pure violuric acid. A method is recommended for the preparation of pure murexide (ammonium purpurate) (compare

Hartley, Trans., 1905, **87**, 1981). The values for the electrical conductivity of the pure salt are: $\mu_{256} = 51 \cdot 2$, $\mu_{512} = 51 \cdot 5$, $\mu_{1024} = 51 \cdot 8$, and $\mu_{\infty} = 52 \cdot 9$. The conductivity of the system: murexide + HCl = purpuric acid + NH_4Cl has been determined at 0°. The purpuric acid is only slowly transformed into uranil and alloxan, and becomes colourless after three days. The initial value for μ_{512} is 225, but this gradually falls to 167 after twenty-five minutes, and to 21 after three days.

The value μ_{∞} for purpuric acid at 0° has been found to be 248·8 from the equation $\underset{278 \cdot 8}{\mu_{\infty}\,HCl} - \underset{82 \cdot 9}{\mu_{\infty}\,NH_4Cl} + \underset{52 \cdot 9}{\mu_{\infty}\,\text{murexide}} = \underset{248 \cdot 8}{\mu_{\infty}\,\text{purpuric}}$ acid. The degree of dissociation at 0° and v_{512} is thus 0·9, and $K = 0 \cdot 0158$.

Alloxan is not regarded as a quinonoid substance, since it shows only general absorption. J. J. S.

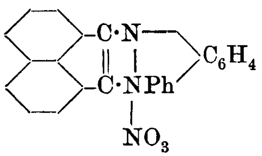
Synthesis of 5 : 7 : 5′ : 7′-Tetrachloroindigotin. ERWIN OBERREIT (*Compt. rend.*, 1910, **150**, 282—283. Compare Danaïla, this vol., i, 137).—The constitution of this substance follows from the fact that it may be prepared from dichloroglycine-*o*-carboxylic acid which has been obtained from 3 : 5-dichloroanthranilic acid. W. O. W.

Quinoline-Red. EDUARD VONGERICHTEN and L. KRANTZ (*Ber.*, 1910, **43**, 128—130).—Quinoline-red is obtained by the interaction of molecular proportions of benzotrichloride, quinaldine, and *iso*quinoline in presence of zinc chloride (Hofmann, Abstr., 1887, 380). When oxidised with potassium dichromate, a base is formed, m. p. 125°, which is regarded as *quinolyl* iso*quinolyl ketone*, $C_9H_6N \cdot CO \cdot C_9H_6N$, since on heating it with concentrated potassium hydroxide, *iso*quinoline and an acid, probably quinaldinic acid, are formed. The base dissolves with a yellow coloration in concentrated acids, and yields an intensely yellow-coloured, crystalline precipitate with phosphorus pentachloride in chloroform solution. The *oxime* forms somewhat grey-coloured, glistening plates, m. p. 245°. A second product of the oxidation is benzaldehyde. E. F. A.

Acenaphthene Series. FRITZ ULLMANN and ERWIN CASSIRER (*Ber.*, 1910, **43**, 439—445).—As acenaphthene is now a commercial product, the authors have attempted to convert it into dyes or into products from which dyes may be obtained.

A 40% yield of naphthalic acid can be obtained by oxidising acenaphthene with sodium dichromate and sulphuric acid (compare Graebe and Gfeller, Abstr., 1892, 863). Naphthastyril (Ekstrand, Abstr., 1886, 715; 1889, 52) is formed when naphthalimide is treated with sodium hydroxide solution and then with sodium hypo chlorite at 15—25°. It reacts with 10% sodium hydroxide solution and *p*-toluenesulphonic chloride, yielding 8-p-*toluenesulphonylaminonaphthoic acid*, $C_7H_7 \cdot SO_2 \cdot NH \cdot C_{10}H_6 \cdot CO_2H$, as colourless needles, m. p. 158—159° (decomp.). With acetic anhydride the acid yields p-*toluenesulphonylnaphthastyril*, $C_{18}H_{13}O_3NS$, as straw-yellow, glistening needles, m. p. 174°.

Phenylacenaphthaphenazonium nitrate (annexed formula), obtained from acenaphthenequinone, α-aminodiphenylamine, and acetic and nitric acids, crystallises in glistening, yellow needles. It dyes cotton mordanted with tannin a pale lemon-yellow. The *zincochloride*, $2C_{24}H_{15}N_2ZnCl_3$, forms yellow plates with a brassy lustre; the *dichromate*, $(C_{24}H_{15}N_2)_2Cr_2O_7$, forms a yellowish-brown, crystalline powder, and the free *base*, $C_{25}H_{15}N_2\cdot OH$, a yellowish-green precipitate. The *methyl ether*, $C_{25}H_{18}ON_2$, forms glistening, yellow crystals, m. p. 180—185°.



3-*Chlorophenylnaphthaphenazonium nitrate*,

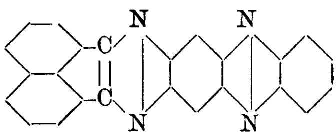
$$C_{10}H_6<\begin{matrix}C\cdot N\text{------}\\ \| \quad | \\ C\cdot NPh(NO_3)\end{matrix}>C_6H_3Cl,$$

obtained from acenaphthenequinone and 5-chloro-2-aminodiphenylamine, forms yellow needles, and dyes cotton mordanted with tannin a yellowish-green. The *methyl ether*, $C_{25}H_{17}ON_2Cl$, forms pale green, glistening plates, and has m. p. 200—220°.

2-*Aminophenyl-acenaphthaphenazonium chloride*,

$$C_{10}H_6<\begin{matrix}C\cdot N\text{------}\\ \| \quad | \\ C\cdot NPhCl\end{matrix}>C_6H_3\cdot NH_2,$$

crystallises in deep violet-coloured needles, and dyes mordanted cotton Bordeaux-red. The *nitrate*, $C_{24}H_{16}O_3N_4$, crystallises in violet plates. The *acetyl* derivative, $C_{26}H_{18}ON_3Cl$, crystallises in long, red needles.



Acenaphthaphenazineazine (annexed formula), obtained by condensing acenaphthenequinone and 2:3-diaminophenazine in acetic acid solution, crystallises in red needles, which are not molten at 320°.

J. J. S.

Methylene-Blue. PAUL LANDAUER and HUGO WEIL (*Ber.*, 1910, **43**, 198—203).—Dürrschnabel has shown (*Diss.*, Giessen, 1907) that indamines, oxazines, thiazines, and other para-quinonoid substances are converted by sulphurous acid or hydrogen sulphite into sulphonated leuco-compounds, whilst ortho-quinonoid substances, such as the indulines and safranines, are not reduced, and usually form sparingly soluble sulphites. The authors find that phenylhydrazine acts in a similar way. Methylene-blue, suspended in alcohol, is treated with phenylhydrazine at the ordinary temperature; after half an hour's warming on the water-bath, the system is allowed to cool in carbon dioxide or coal gas. Nitrogen is evolved, and leucomethylene-blue, m. p. 185°, is obtained in yellow needles. The leuco-compound is stable in dry oxygen, and in the presence of alkaline oxidising agents can be directly acetylated by acetic anhydride, and yields a yellow *sodium* salt with alcoholic sodium ethoxide. Methylene-green by similar treatment yields brown needles of *nitroleucomethylene-blue*, $C_{16}H_{18}O_2N_4S$, m. p. 146—147°.

C. S.

Synthesis of Hetero-condensed, Heterocyclic Compounds with Two Nuclei. Derivatives of 2-Methyl-1 : 3-triazo-7 : 0′-pyrimidine [2-Methyl-1 : 3 : 7 : 9-benztetrazole] from 5-Amino-2-methyl-1 : 3 : 4-triazole. CARL BÜLOW and KARL HAAS (*Ber.*, 1910, **43**, 375—381. Compare Abstr., 1909, i, 614, 615 (and Errata), 1470; this vol., i, 80, 81).—5-Amino-2-methyl-1 : 3 : 4-triazole contains a labile hydrogen atom attached to the nitrogen next the basic group. Accordingly, it interacts with 1 : 3-diketones, forming di- and tri-alphyl or aryl derivatives of 2-methyl-1 : 3 : 7 : 9-benztetrazole, or with keto-esters, forming methyl benztetrazolehydroxylic acid derivatives.

2 : 4 : 6 - *Trimethyl* - 1 : 3 : 7 : 9 - *benztetrazole*, $\begin{array}{l} \text{CMe}{=\!=}\text{N}\cdot\text{C}\colon\text{N} \\ \text{CH}\colon\text{CMe}\cdot\text{N}\cdot\text{N} \end{array}\!\!>\!\text{CMe}$, prepared by interaction of the aminotriazole with acetylacetone, forms colourless needles, m. p. 141—142°.

2 : 4 : 5 : 6-*Tetramethyl*-1 : 3 : 7 : 9-*benztetrazole*, $\begin{array}{l} \text{CMe}{=\!=}\text{N}\cdot\text{C}\colon\text{N} \\ \text{CMe}\colon\text{CMe}\cdot\text{N}\cdot\text{N} \end{array}\!\!>\!\text{CMe}$, obtained in a similar manner from methylacetylacetone, has m. p. 116—117°.

4-*Phenyl*-2 : 6-*dimethyl*-1 : 3 : 7 : 9-*benztetrazole* forms colourless, radially grouped, long, thin prisms, m. p. 110—111°.

4-*Hydroxy*-2 : 6-*dimethyl*-1 : 3 : 7 : 9-*benztetrazole*,

$$\begin{array}{l} \text{CMe}{=\!=}\text{N}\cdot\text{C}\colon\text{N} \\ \text{CH}\colon\text{C(OH)}\cdot\text{N}\cdot\text{N} \end{array}\!\!>\!\text{CMe},$$

obtained by boiling aminomethyltriazole with ethyl acetoacetate in glacial acetic acid solution, separates in glistening crystals, m. p. above 280°. This and the following compounds are acidic, forming salts with alkalis. These react neutral in aqueous solution, and give amorphous or crystalline precipitates with salts of the heavy or alkaline-earth metals. Thus the *lead* salt forms short plates; the *copper* salt, bright green needles; the *zinc* salt, stellar aggregates of needles; the *calcium* salt, glistening needles.

4-*Hydroxy*-2 : 6-*dimethyl*-5-*ethyl*-1 : 3 : 7 : 9-*benztetrazole*, prepared from ethyl ethylacetoacetate, has m. p. 262°, and forms soluble neutral salts, which are not decomposed by carbon dioxide.

4-*Hydroxy*-6-*phenyl*-2-*methyl*-1 : 3 : 7 : 9-*benztetrazole*, obtained from ethyl benzoylacetate, forms long, colourless needles, which do not melt at 293°. E. F. A.

Yellow and Red Forms of Salts and Hydrates of Hydroxy-azo-derivatives. ARTHUR HANTZSCH and PHILIP W. ROBERTSON (*Ber.*, 1910, **43**, 106—122. Compare Tuck, Trans., 1907, **91**, 450; Gorke, Köppe, and Staiger, Abstr., 1908, i, 477).—The salts of hydroxy-azo-compounds appear to exist in yellow and red modifications similar to the yellow and red salts of nitrophenols. It is only in the case of silver salts that yellow and red isomeric salts have been obtained from the same compound. Salts of the type $R\cdot N_2\cdot C_6H_4\cdot OM + 0\cdot5MeOH$ ($EtOH$, $CH_3\cdot CO_2Et$, $COMe_2$, or C_5H_5N) are common; they are orange-coloured, and are regarded as compounds of 1 mol. of red salt, 1 mol. of yellow salt, and 1 mol. of the crystallising medium. When the last is removed, they yield red or yellow salts, or, sometimes, orange-coloured salts.

The following table gives the colours of the salts of four hydroxyazo-compounds :

	Benzene-azophenol.	p-Chlorobenzene-azophenol.	p-Bromobenzene-azophenol.	Benzene-azo-o-di-bromophenol.
H.........	Yellow	Yellow	Yellow	Orange
Li	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Na	Orange	Orange	Orange	Yellow
K.........	Red	Pale red	Red	Orange
Rb	Dark red	Orange	Red	Orange
Cs	Pale red	Red	Red	Orange
Ag	Yellow (stable) Red (labile)	Yellow (stable) Red (labile)	Yellow (stable) Red (labile)	Red

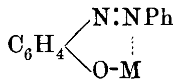
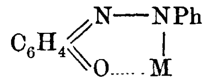
It is noticeable that the lithium salts are paler in colour than the original hydroxy-derivatives, and that, as a rule, the caesium salts are paler than the rubidium.

The hydrates of hydroxyazo-compounds also appear as representatives of two chromo-isomeric series.

The following are the colours of the hydroxyazo-compounds and of their hydrates (0·5 or 1 mol. H_2O) : o-Chlorobenzeneazophenol, red, yellow ; meta-compound, yellow, red ; para-compound, yellow, yellowish-red ; o-bromobenzeneazophenol, red, yellow ; meta-compound, yellow, red ; para-compound, yellow, red ; o-tolueneazophenol, yellow, yellow ; meta-compound, yellow, yellow ; benzeneazo-m-cresol, yellow, yellow ; m-chlorobenzeneazo-m-cresol, yellow, red ; o-tolueneazo-m-cresol, yellowish-red, yellowish-red ; benzeneazo-o-chlorophenol, yellowish-red (labile), yellow (stable), yellowish-red. The last-mentioned colour in each case refers to that of the hydrate.

The determinations of the absorption spectra and of the molecular extinctions of solutions of the salts and hydrates show that the yellow and red forms are not polymorphous or polymeric. The solutions in indifferent solvents have much the same colours as the solid salts. The nature of the solvent also affects the colour of the solutions, the more positive the nature of the solvent (namely, pyridine) the deeper the colours. These solutions of salts of hydroxyazo-compounds are regarded as equilibrium mixtures of yellow and red salts, just as in the case of the violurates. From such solutions the orange-coloured additive compounds (1 mol. yellow, 1 mol. red, 1 mol. solvent) separate, as they are sparingly soluble. All these solid additive compounds have practically the same colour, so that the effect of different solvents on the solids is practically nil ; since, however, the solutions have different colours it is probable that the relative amounts of red and yellow salts in the different solutions vary considerably. The increase in colour of the salts, as compared with the free hydroxy-compounds, indicates that salt formation as a rule favours the formation of the red form. It is shown that mere salt formation (Gorke) has not necessarily an auxochromic effect, since lithium salts are paler than the free hydroxy-compounds, and dipropylamine salts in some cases give absorption curves exactly analogous to those of the free hydroxy-compounds.

The following structural valency formulæ are suggested for the yellow and red forms :

 and  ,

where the dotted lines represent subsidiary valencies.

The following values for the molecular extinctions ($\lambda = 546$) of hydroxyazobenzene and its salts in different media at 15° and $V = 200$ are given :

Rubidium salt in pyridine 510, in ethyl acetate 81, in alcohol 44 ; cæsium salt in alcohol 24, in benzene + 4% alcohol 18, in hexane + 4% alcohol 14 ; lithium salt in ether 12 ; dipropylamine salt + 100 mols. dipropylamine in benzene 9 ; hydroxyazobenzene in carbon tetrachloride 8, in chloroform 7, in pyridine 7, in benzene 7, in alcohol 4. The values for the molecular extinctions ($\lambda = 546$) for salts of dibromohydroxyazobenzene at 15° and $V = 400$ are :

Solvent.	Li.	Na.	K.	Rb.	Cs.
Ether	15	17	18	18	—
Alcohol	39	37	35	35	36
Pyridine.........	140	179	180	210	220

J. J. S.

Formation and Decomposition of Symmetrical Bisazo-compounds of Ethyl Arylhydrazonemesoxalylbishydrazone-acetoacetates and of Ethyl Malonylbishydrazoneaceto-acetate. Carl Bülow and C. Bozenhardt (*Ber.*, 1910, **43**, 234—242).—Ethyl malonylbishydrazonebenzeneazoacetoacetate reacts with one molecule of benzenediazonium chloride, yielding ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate with 72% yield (compare Abstr., 1908, i, 253). In addition, small quantities of ethyl benzeneazoacetoacetate, *cyclo*malonylhydrazide, and 4-benzeneazo-3-methyl-5-pyrazolone are formed. Ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate, when warmed with phenylhydrazine, decomposes into 4-benzeneazo-1-phenyl-3-methylpyrazolone (orange needles, m. p. 154—155° ; yield 85%), 4-*benzeneazopyrazolidone* (m. p. 266°), and hydrazine. When boiled with dilute potassium hydroxide, it yields 4-benzeneazo-3-methyl-5-pyrazolone and mesoxalic acid-phenylhydrazone ; whilst by the action of boiling acetic acid 4-benzeneazo-3-methyl-5-pyrazolone, ethyl benzeneazoacetoacetate, and 4-benzeneazo-3 : 5-pyrazolidone are produced. Dimethyl mesoxalate-phenylhydrazone (compare Abstr., 1905, i, 90), when treated with hydrazine hydrate, yields *mesoxalylphenylhydrazonedihydrazide*, m. p. 164°. The *diacetyl* derivative has m. p. 246—247°. The dihydrazide condenses with ethyl benzeneazoacetoacetate, giving ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate, the constitution of which is confirmed by this mode of preparation. The above dihydrazide when boiled with acetic acid also yields 4-benzeneazo-3 : 5-pyrazolidone of m. p. 266°, already mentioned. Ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate is also produced by condensing equimolecular quantities of benzenediazonium chloride and *ethyl malonylbishydrazonebenzeneazoacetoacetate*. The latter is

formed in 80% yield by the condensation of 2 molecules of ethyl benzeneazoacetoacetate with malonyldihydrazide. It is decomposed by boiling alcohol into ethyl malonate and 4-benzeneazo-3-methyl-5-pyrazolone. On heating, it melts at 128°, then gas is evolved, and the mass solidifies, melting again at 217—218°. In this process the theoretical quantity of alcohol is evolved, and the residue consists of 4-benzeneazo-3-methyl-5-pyrazolone and 1 : 1-*malonylbis*-4-*benzeneazo*-3-*methyl*-5-*pyrazolone* (compare Abstr., 1907, i, 986), m. p. 225·5°. On boiling with potassium hydroxide or pyridine, the latter yields 4-benzeneazo-3-methyl-5-pyrazolone and malonic acid.

Ethyl malonylbishydrazoneacetoacetate yields with 3 molecules of *p*-diazotoluene chloride, *ethyl*-p-*tolylhydrazonemesoxalylbishydrazonetoluene*-p-*azoacetoacetate*, orange needles, m. p. 209—210°. By the condensation of malonyldihydrazide with ethyl toluene-*p*-azoacetoacetate, *ethyl malonylbishydrazonetoluene*-p-*azoacetoacetate*, orange needles, m. p. 114—115°, is produced. R. V. S.

Azo-dyes derived from 2 : 4-Dimethylpyrrole and Hæmopyrrole. LEON MARCHLEWSKI and J. ROBEL (*Ber.*, 1910, **43**, 260—266 *).—For the purpose of comparison with the azo-dyes obtained from hæmopyrrole and chlorophyllpyrrole, the authors have investigated the diazotisation of dimethylpyrrole. In addition to the monoazo-derivative of Plancher and Soncini (Abstr., 1901, i, 432), they have obtained small quantities of a *substance*, $C_{24}H_{25}N_6Cl$, which they suppose to have the formula : $(N_2Ph \cdot C_6H_7N \cdot C_6H_7N \cdot N_2Ph)HCl$. It crystallises in well-developed red needles having a metallic lustre, and it is only slightly soluble in most solvents. In physical characteristics (including the absorption spectrum) the substance shows similarity to the azo-derivative of hæmopyrrole. R. V. S.

Reduction of Nitroso-derivatives of Acetyl- and Benzoylhydrazobenzene. LOUIS NOMBLOT (*Compt. rend.*, 1910, **150**, 338—339).—*Nitrosoacetylhydrazobenzene*, NAcPh·NPh·NO, obtained by adding ethyl nitrite to acetylhydrazobenzene suspended in alcohol, occurs in yellow prisms, m. p. 65°. The corresponding *benzoyl* derivative crystallises in pale yellow leaflets, m. p. 116·5°. The action of reducing agents on these two substances has been studied. An alcoholic solution of hydrazine hydrate converts them into the corresponding acidylhydrazobenzene, with liberation of ammonia. Aluminium amalgam gives aniline, together with acetanilide or benzanilide. Zinc dust in presence of acetic acid at 0—5° gives no reduction products. Under no conditions were triazan derivatives obtained. W. O. W.

[Preparation of *p*-Aminophenyl-2-azimino-5-naphthol-7-sulphonic Acid.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 214658).—p-*Aminophenyl*-2-*azimino*-5-*naphthol*-7-*sulphonic acid*, a grey, crystalline powder sparingly soluble in water and employed in the production of Bordeaux-red dyes, is prepared by the following series of operations:

1-Chloro-2 : 4-dinitrobenzene is condensed with β-naphthylamine-

* and *Bull. Acad. Sci. Cracow*, 1910, *A*, 1—8.

5 : 7-disulphonic acid, yielding 2 : 4-dinitrophenyl-β-naphthylamine-5 : 7-disulphonic acid; this is reduced with sodium sulphide and ammonium chloride to p-*nitro*-o-*aminophenyl*-β-*naphthylamine*-5 : 7-*disulphonic acid*, the *disodium* salt of which forms red, crystalline leaflets. This substance is treated with sodium nitrite in the presence of sulphuric acid, and the resulting *nitroazimino*-compound reduced with iron filings to p-*aminophenyl*-2-*aziminonaphthalene*-5 : 7-*disulphonic acid*, grey needles, which, on heating with sodium hydroxide solution at 180—190°, yields the foregoing naphtholsulphonic acid.

F. M. G. M.

Azoarylhydrazinesulphonic Acids. JULIUS TRÖGER and A. WESTERKAMP (*Arch. Pharm.*, 1909, **247**, 657—698).—The hydrazinesulphonic acid, obtained by the action of sulphur dioxide on aqueous benzenediazonium sulphate (Abstr., 1904, i, 118; 1906, i, 120, 993, 994), has been synthesised by Troeger and Puttkammer (Abstr., 1907, i, 263) by converting diazotised aminoazobenzene into azobenzenediazosulphonate, and reducing the latter by ammonium sulphide:

$$N_2Ph\cdot C_6H_4\cdot NH_2 \longrightarrow N_2Ph\cdot C_6H_4\cdot N_2Cl \longrightarrow \underset{\text{(Labile salt.)}}{N_2Ph\cdot C_6H_4\cdot N_2\cdot O\cdot SO_2K}$$

$$\longrightarrow \underset{\text{(Stable salt.)}}{N_2Ph\cdot C_6H_4\cdot N_2\cdot SO_3K} \longrightarrow N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H.$$

This synthetic process has now been applied to numerous aminoazo-compounds, whereby hydrazinesulphonic acids are obtained, which are red, blue, violet, or brown; they are best purified by means of their salts with aromatic amines, and are reduced by stannous chloride and hydrochloric acid in the sense of the equation:

$$N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H + 6H + H_2O = NH_2Ph + NH_2\cdot C_6H_4\cdot NH_2 + NH_3 + H_2SO_4,$$

a monoamine and a diamine always being formed. When heated with alcoholic hydrogen chloride and an aldehyde or ketone, the hydrazinesulphonic acids lose the sulphonic acid group, and are converted into hydrazones which form coloured salts with the hydrochloric acid.

4-Amino-*o'm*-azotoluene thus yields a reddish-brown o'm-*azotoluene*-4-*hydrazinesulphonic acid*, $C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot NH\cdot SO_3H$ (the *potassium* and *barium* salts are described; the p-*toluidine* salt,

$$C_{14}H_{15}N_4\cdot SO_3\cdot NH_3\cdot C_7H_7,$$

m. p. 158°, forms yellow needles), which yields *o*-toluidine and 1 : 2 : 5-tolylenediamine by reductive fission, and in the presence of alcoholic hydrogen chloride reacts with salicylaldehyde to form o-*hydroxybenzylidene*-o'm-*azotoluene*-4-*hydrazone*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH,$$

m. p. 130—131° (the *hydrochloride*, $C_{21}H_{21}ON_4Cl$, forms violet needles, and the *sulphate*, blue needles with a green reflex), with *p*-nitrobenzaldehyde to form a similar *hydrazone*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot N:CH\cdot C_6H_4\cdot NO_2,$$

m. p. 158°, with *p*-methoxybenzaldehyde to form the reddish-yellow

hydrazone, $C_{22}H_{22}ON_4$, m. p. 147°, and with benzaldehyde to form an orange-red *hydrazone*, $C_{21}H_{20}N_4$, m. p. 160°.

4-Amino-*mp'*-azotoluene yields reddish-brown, amorphous mp'-*azotoluene-4-hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, the p-*toluidine* salt of which, m. p. 183°, forms yellow needles; the *hydrazone*, $C_{22}H_{22}ON_4$, m. p. 148°, from *p*-methoxybenzaldehyde forms golden-yellow leaflets; the *hydrazone*, $C_{21}H_{20}ON_4$, m. p. 120—121°, from salicylaldehyde forms red prisms, and the *hydrazone*, $C_{21}H_{19}O_2N_5$, m. p. 176—177°, from *m*-nitrobenzaldehyde is a reddish-brown, crystalline powder.

op'-*Azotoluene-4-hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, obtained from 4-amino-*op'*-azotoluene, is a dark reddish-brown, amorphous powder; the p-*toluidine* salt, m. p. 171°, forms reddish-yellow needles. mp'-*Azotoluene-6-hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, is an indigo-blue, amorphous powder obtained from 6-amino-*op'*-azotoluene; the p-*toluidine* salt has m. p. 154°, and the *aniline* salt has m. p. 139°. *Benzeneazo-*p*-toluene-4-hydrazinesulphonic acid*,

$$C_{13}H_{14}O_3N_4S,$$

is a dark red, amorphous powder, which forms a yellow, crystalline p-*toluidine* salt, m. p. 170° (decomp.), and a p-*xylidine* salt, m. p. 175° (decomp.). *Benzeneazo-*p*-xylidine*, $N_2Ph\cdot C_6H_2Me_2\cdot NH_2$, m. p. 104—105°, obtained by the slow addition of diazotised aniline hydrochloride to an alcoholic solution of *p*-xylidine and treatment of the resulting hydrochloride with ammonium hydroxide, separates from dilute alcohol in golden leaflets, and from petroleum and benzene as a deep orange, crystalline powder, and forms a *nitrate* crystallising in long, blue needles, a violet *hydrogen sulphate*, and a golden-yellow *oxalate*. It is converted by the usual processes into *benzeneazo-2 : 5-xylene-4-hydrazinesulphonic acid*, $C_{14}H_{16}O_3N_4S$, a dark red, micro-crystalline powder, the reddish-yellow p-*toluidine* salt of which has m. p. 158°.

Benzeneazo-α-naphthylhydrazinesulphonic acid,

$$N_2Ph\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3H,$$

obtained from benzeneazo-α-naphthylamine, is an amorphous, violet powder, which is best purified by means of its *potassium* salt,

$$C_{16}H_{13}O_3N_4SK,$$

which crystallises in reddish-yellow needles. The acid is reduced by zinc dust and hot acetic acid, yielding aniline and 1 : 4-naphthylenediamine, and reacts with alcoholic hydrogen chloride and aldehydes in the manner mentioned, hydrazones being produced in the form of hydrochlorides; the *hydrazone*, $N_2Ph\cdot C_{10}H_6\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OMe$, m. p. 158—160°, from *p*-methoxybenzaldehyde forms orange needles (*hydrochloride*, deep blue needles); the *hydrazone* from salicylaldehyde has m. p. 205° (*hydrochloride*, bluish-violet needles); the *hydrazone* from *p*-nitrobenzaldehyde has m. p. 172—173° (*hydrochloride*, dark green powder).

In a similar manner, benzeneazo-β-naphthylamine yields *benzene azo-β-naphthylhydrazinesulphonic acid*, a coffee-coloured, amorphous powder, which is purified through the p-*toluidine* salt, m. p. 165° (decomp.).

2 : 4 : 3' : 5'-*Tetramethylazobenzene-2-hydrazinesulphonic acid*,

$$C_6H_3Me_2\cdot N_2\cdot C_6H_2Me_2\cdot NH\cdot NH\cdot SO_3H,$$

obtained from aminoazo-*m*-xylene, is a red, amorphous powder, which forms a p-*toluidine* salt, m. p. 170° (decomp.), *aniline* salt, m. p. 153° (decomp.), and a p-*xylidine* salt, m. p. 176° (decomp.).

a-Naphthylazo-a-naphthylhydrazinesulphonic acid,

$$C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot NH \cdot SO_3H,$$

obtained from aminoazo-a-naphthalene, is a dark blue substance.

C. S.

The Adsorption of Proteins. WILHELM BILTZ and HANS STEINER (*Biochem. Zeitsch.*, 1909, **23**, 27—42) —The adsorption of egg-white by cellulose, iron hydroxide, and kaolin was estimated in varying concentrations of the protein. The amount adsorbed was determined by estimating the nitrogen in the clear solution, after filtration of the adsorbent, by a modification of Kjeldahl's method, the amount of ammonia being determined colorimetrically with the use of Nessler's reagent. The adsorption process is not entirely reversible, and the results do not entirely agree with the ordinary adsorption equation. The application of the adsorption formula to the combination of toxin and antitoxin was also investigated ($1 - T/n = \log k + 1/p \log T$, where T is the concentration of the free toxin, and $1 - T$ that of the combined). The results of the neutralisation of tetanolysin and streptolysin by the antilysins, and of the streptolysin by cholesterol, of diphtherotoxin by its antitoxin, of saponin by ox-blood, of cobralysin by antivenin, and other similar reactions were investigated. The results obtained were compared with those calculated from the adsorption equation and Arrhenius' mass reaction equation. Neither of these equations agreed in a satisfactory manner with the results obtained experimentally.

S. B. S.

Composition of the Products of the Alkaline Hydrolysis of Crystalline Egg-albumin. NOGENDRAMOHON GUPTA (*Monatsh.*, 1909, **30**, 767—771).—The products resulting from the hydrolysis of egg-albumin by sodium hydroxide (compare Skraup and Hummelburger, Abstr., 1909, i, 340) have been submitted to careful analysis, with the following results :

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.
Protalbic acid	55·4	7·2	14·3	2·4
Lysalbic ,, ...	52·9	7·0	14·9	1·2
Lysalbinpeptone	46·2	6·6	10·3	1·2

W. H. G.

The Preparation and Properties of Iodo-Mucoids. GUSTAVE M. MEYER (*J. Biol. Chem.*, 1909, **7**, 11—16).—Iodo-mucoids were prepared by the action of iodine on tendo-mucoid in a dilute solution of sodium carbonate; they contain approximately 14% of iodine.

W. D. H.

The Relation of Proteins to Crystalloids. I. The Osmotic Pressure of Hæmoglobin and the Laking of Red Blood-corpuscles. HERBERT E. ROAF (*Quart. J. exp. Physiol.*, 1910, **3**, 75—96).—A simple method is described for the direct measurement of the osmotic pressure of a solution when the solute does not pass

through parchment paper or other suitable membranes. In this way the osmotic pressure of laked corpuscles and crystallised hæmoglobin was measured, and pressures corresponding with the molecular weight of hæmoglobin calculated from other data were obtained if conditions obtain which limit ionisation; but otherwise much higher pressures are reached, and it is suggested that this is due to the ionising of hæmoglobin salts; both acid and alkali increase the pressure, and as with serum proteins, a minimal pressure is found near the neutral point. Many substances lower the osmotic pressure, and thus might help to prevent laking of red corpuscles. Pressures were obtained with corpuscles laked by freezing and thawing up to 282 and 256. If ionisation occurred, the calculated pressure might be as high as 960 mm. of mercury. With such a range of pressure, the osmotic pressure of hæmoglobin should be considered in discussing the laking of corpuscles, but until further experiment has determined the pressures in mixed solutions containing the various crystalloids of the corpuscle, it cannot be decided what part is played by hæmoglobin and how much is due to other factors. W. D. H.

Blood Colouring Matter. WILLIAM KUSTER (*Ber.*, 1910, **43**, 370—375).—The compound, $C_{36}H_{36}O_3N_4$, obtained by Küster and Fuchs (Abstr., 1907, i, 572) as a bye-product of the action of aniline on hæmin is also formed in small quantity when acetylhæmin is converted into dehydrochloridehæmin. By the action of concentrated hydrochloric acid under pressure on hæmatin, the organic material partly loses its acid properties and partly undergoes oxidation. Hæmin and hæmatin are regarded as ferric compounds, and the ferric chloride formed oxidises part of the iron-free hæmatin. The oxidation product does not undergo rearrangement to hæmatoporphyrin. When hydrogen bromide is used, the oxidising action of the ferric bromide is neutralised, and hæmatoporphyrin formation takes place. Ten % hydrochloric acid only eliminates 5% of the iron from hæmin at 130°, whereas under similar conditions over 90% of the iron is separated from hæmatin.

Hæmatin is slowly changed by solution in alkali, whereas the fresh solution is completely precipitated by the theoretical quantity of barium chloride. After keeping, a large excess of this is required. Polymerisation to a β-hæmatin takes place on keeping.

The conversion of hæmatin by reducing agents into hæmochromogen is regarded as corresponding with a reduction from the ferric to the ferrous state. Hæmoglobin contains ferrous iron; oxyhæmoglobin, however, contains iron peroxide.

Hæmin forms salts with 3 mols. of alkali hydroxide; dehydrochloridehæmin, salts with 2 mols. These can be dialysed in 1% solution without the dye passing through. Hæmin only takes up 2 mols. of sodium carbonate, and sodium hydrogen carbonate appears in the outer water on dialysis. Precipitates obtained with other metallic salts showed a very varying metal content.

The iron salts dissolve in sodium hydroxide and are acids; seemingly, the second iron atom is attached to the free nitrogen atom.

E. F. A.

Behaviour of Gelatinous Substances or Collains towards Carbon Disulphide. Wl. S. Sadikoff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1597—1686; *Kolloid. Chem. Beihefte*, 1910, 1, 119—220).—When an alkali acts on glutin in presence of carbon disulphide, "thiohydration" occurs, this consisting of two distinct processes, namely, hydration by the alkali and subsequent addition of carbon disulphide or "thionylation" (compare Abstr., 1907, i, 740). The most characteristic part of the thionylglutin thus obtained is the complex to which the carbon disulphide is added, and which is termed the "receptor." This receptor is extremely indifferent, neither being destroyed by water, reacting with tannin, bromine, aldehydes, or the majority of organic acids, nor being replaced by benzoyl chloride or methyl iodide. It takes up carbon disulphide in neutral, alkaline, or acid media, combines with strong mineral acids, and with acetic and oxalic acids, is substituted by trinitrophenol and "immobilised," or rendered incapable of taking up carbon disulphide, by solutions of sulphates, probably owing to the sulphuric acid formed by adsorptive decomposition of the salts.

In the case of tendo-collagen, the receptor is not homogeneous. The predominating part of it is readily reactive, being replaced by carbonic acid, and by organic and mineral acids, acetic anhydride, benzoyl chloride, bromine, methyl iodide, or aldehydes; it is stable towards the action of heat or water, and is not replaced by picric acid. The lesser part of the receptor is highly inert, is replaceable only by mineral acids and tannin, and is stable towards the action of water, but thermo-labile; this part is not altered by the action of alkali hydroxide. The reactive portion of this receptor would seem to be a primary or secondary amine. T. H. P.

The Scission Products Resulting from the Partial Hydrolysis of Proteins. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1909, **63**, 401—404).—From the partial hydrolysis of silk, glycyl-*l*-tyrosine was obtained previously. The present research gives details of the preparation and identification of another dipeptide from the same source, namely, *d*-alanyl-glycine. W. D. H.

Trypsin and Antitrypsin. Kurt Meyer (*Biochem. Zeitsch.*, 1909, **23**, 68—92).—Samples of dried pancreatic juice and juice from the small intestine were used in the experiment, and dissolved to give the necessary concentrations as required. The tryptic action was estimated by the Gross-Fuld caseinogen method. The influence of the quantity of kinase on the activation of the trypsinogen was first investigated. The results indicate that the kinase action is of ferment-like character. The grade of activation is not proportional to the amount of kinase, and very small quantities of the latter can activate large quantities of the trypsinogen, provided that sufficient time is allowed for the action. The rate of activation is approximately proportional to the amount of kinase. The greater activity of mixtures containing large amounts of kinase is apparently due to a shortening of the activating process, owing to which the concurrent destruction of the trypsin and kinase becomes less marked. An excess of kinase does not inhibit the activation. The inhibitory

substance of the serum is neither an antikinase nor an anti-trypsinogen. The former possibility is excluded by the fact that the anti-action is not overcome by the addition of excess of kinase, and is also exerted on trypsin which has been obtained from trypsinogen by calcium salts. Antitrypsinogen and antikinase are also excluded by the fact that the inhibitory action of the serum is not increased by allowing it to act on the kinase or trypsinogen alone before mixture, and that the quantity necessary for inhibiting a mixture which is being gradually activated depends on the amount of trypsin actually present at the time of addition.

No antitrypsinogen or antikinase could be obtained by immunisation experiments. The saturation of trypsin by the anti-substance follows the law of multiple proportions. In the fractional saturation of trypsin by the anti-substance, the Danysz phenomenon was observed, namely, the inhibitory action is weaker than if the whole quantity of anti-substance had been added at one time.

Previous treatment of trypsin by antitrypsin did not increase the inhibitory effect. The formation of a non-digesting, but anti-substance binding trypinoid could not be effected. The effect of heating trypsin and the anti-substance was also investigated. The results indicate that antitrypsin is not a negative catalyst, but actually enters into combination with trypsin. No kind of specificity was noted in the case of antitrypsin. S. B. S.

Influence of the Reaction of the Medium on the Filtration of Diastases. MAURICE HOLDERER (*Compt. rend.*, 1909, **149**, 1153—1156).—Details of experiments on extracts of *Aspergillus niger* are given, from which it appears that a porcelain filter is permeable to sucrase when the solution in which this is present is neutral to phenolphthalein; when the solution is neutral to methyl-orange, however, the ferment no longer passes the filter. In order, therefore, to render the extraction of sucrase more complete, it is desirable to have the solution alkaline whilst maceration is in process. W. O. W.

Influence of the Reaction of the Medium on the Filtration of Malt Enzymes. MAURICE HOLDERER (*Compt. rend.*, 1910, **150**, 285—288. Compare preceding abstract).—The enzymes of malt, amylase, dextrinase, and peroxydiastase resemble the diastases already studied in their behaviour when the solutions are filtered through porcelain. Filtration occurs readily when the solutions are neutral to phenolphthalein, but the passage of the enzymes through the filter is inhibited if the medium is neutral to methyl-orange. W. O. W.

Cellase and the Diastatic Decomposition of Cellose. GABRIEL BERTRAND and MAURICE HOLDERER (*Compt. rend.*, 1909, **149**, 1385—1387).—An attempt to ascertain whether a specific ferment exists capable of hydrolysing cellose. Maltase and sucrase are without action on this substance, whilst a maceration of *Aspergillus niger* converts it completely into dextrose. Preparations of emulsin from almonds, and of emulsin with trehalase from barley or malt, have the same action. W. O. W.

Organic Chemistry.

Action of Magnesium on the Vapours of Organic Compounds. EDWARD H. KEISER and LEROY MCMASTER (*J. Amer. Chem. Soc.*, 1910, 32, 388—391).—Keiser and Breed (Abstr., 1895, i, 405) have shown that when the vapour of an aliphatic alcohol was passed over heated magnesium, a black residue was obtained, which was decomposed by water with evolution of hydrogen and allylene. In a later paper (Keiser, Abstr., 1896, i, 457) an account was given of the action of magnesium on the vapours of other compounds. It was found that if the metal was heated in an atmosphere of carbon monoxide or dioxide, a hard mass was obtained, which gave only small quantities of allylene when treated with water, and the conclusion was therefore drawn that a magnesium compound of allylene was probably present in the black residue.

Attempts have now been made to prove definitely whether the substance which yields the allylene is a magnesium allylide or merely a carbide. Experiments have been made with various classes of organic compounds, including paraffin and benzene hydrocarbons, aliphatic acids and esters, aromatic alcohols, halogen derivatives, acetylene, and cyanogen. In each case the residue obtained was treated with water containing a little ammonium chloride, and the gases evolved were led into an ammoniacal solution of silver nitrate. The silver precipitates were analysed, and the results are tabulated.

In all cases in which the magnesium was heated with the vapour of a compound containing hydrogen, the unsaturated hydrocarbon formed was mostly allylene. When the compound did not contain hydrogen, as in the cases of cyanogen and carbon monoxide, only very small quantities of the unsaturated hydrocarbon were produced, but even then the gas evolved contained some allylene as well as acetylene. This fact seemed to indicate that a carbide is produced which yields allylene on treatment with water. Since, however, it was found that the magnesium powder contained hydrogen, and that only a very small quantity of allylene is obtainable from carbon compounds which do not contain hydrogen, the conclusion is drawn that it is not a carbide, but an allylide, which yields the allylene. This is supported by the fact that when magnesium is heated in acetylene, the black residue on treatment with water gives both allylene and acetylene.

E. G.

The Electrochemical Preparation of Chloroform. B. WÄSER (*Chem. Zeit.*, 1910, 34, 141—142).—Chloroform is not obtained in satisfactory yield by the electrolysis of potassium or calcium chloride in presence of alcohol. Barium chloride gives better results, owing to the greater solubility of barium than of calcium hydroxide. A special apparatus is described, in which a porous cylinder surrounds the platinum cathode. The anode is a platinum plate. The cathode

solution is 30 c.c. of hydrochloric acid, D 1·19; the anode solution contains 80 grams of barium hydroxide, 1 gram of barium chloride, and 300 c.c. of water; 30 c.c. of alcohol are then added slowly, the temperature being 50°. Chloroform and alcohol distil off together, the temperature being gradually raised to 70°. The cathode solution is renewed from time to time. The anode current density is about 4 amperes per sq. dm., and the current efficiency is about 35%. Barium carbonate must be absent. Acetone gives a lower yield than alcohol. C. H. D.

Physical and Physiological Properties of Tetrachloroethane and Trichloroethylene. VICTOR H. VELEY (*Proc. Roy. Soc.*, 1910, *B*, **82**, 217—225).—*Tetrachloroethane.*—The commercial product was fractionally distilled with a Young's still-head with three bulbs, and the portion of b. p. 147·2° was taken as pure. The densities found were $D_4^4 = 1·6208$ and $D_{17}^{17} = 1·6013_0$. Determinations of the refractive index, μ_D, made at temperatures 15·2° to 17·3°, and corrected to a standard temperature 17°, gave as final value $1·495587 \pm 0·0_56$, calculated by Bessel's function. Gladstone's factor $\mu - 1/d = 0·3095$, and Lorenz's factor $\mu^2 - 1(\mu^2 + 2)d = 0·1824$, which multiplied by the molecular weight give 53·0 and 30·7 respectively.

Trichloroethylene.—One sample after purification boiled at 87·4 ±0·1 (corr.), and another at 87·55±0·1 (corr.). Practically no hydrogen chloride is given off during distillation. Densities at different temperatures: $D_4^4 = 1·4904_5$, $D_{17·5}^{17·5} = 1·4702_0$, $D_{25·5}^{25·5} = 1·4598_7$, the relative volumes being $V_4 = 1$, $V_{17·5} = 1·0128$, $V_{25·5} = 1·0209$. Refractive index, μ_D, determinations at the same temperatures and above give as final value reduced to 17°, $1·479141 \pm 0·0_53$; Gladstone's factor $= 0·326$, and Lorenz's factor $= 0·193$; multiplied by the molecular weight, the results are 42·7 and 25·8 respectively.

Tetrachloroethane is four times more toxic than chloroform, molecule for molecule, but recovery from anæsthesia or paralysis is more regular in the case of the former than in that of the latter.

Trichloroethylene is 1·5 times more toxic than chloroform, molecule for molecule, or 1·36 times weight for weight. Not only the course of abolition, but also of recovery, is much more regular than in the case of chloroform. E. J. R.

Grignard's Reagent and the Barbier-Grignard Reaction. EYVIND BÖDTKER (*Chem. Zeit.*, 1910, **34**, 150).—Attention is called to the fact that the reaction between alkyl iodides and other compounds in presence of magnesium was first employed by Barbier (Abstr., 1899, i, 323), at whose suggestion Grignard studied the reaction, and then devised the reagent in its present form. C. H. D.

The Oxidation Products of Erythritol (*d-l*-Erythronic Acid and *d-l*-Hydroxyerythronic Acid). CARL NEUBERG (*Biochem. Zeitsch.*, 1910, **24**, 166—170).—The erythritol was oxidised by nitric acid. The calcium salts were formed, and the concentrated solution of the latter dropped into alcohol. The calcium salt of the hydroxy-acid remains partly in solution, whereas the calcium salt of the

erythronic acid is precipitated. The calcium salt is then dissolved in water, concentrated barium hydroxide added, and the mixture warmed. The remainder of the hydroxy-acid is precipitated. The mother liquor contains the erythronic acid, which is purified by conversion into the copper salt, and finally into the calcium salt again, which latter, when pure, crystallises. The hydroxy-acid is purified by first obtaining it in the form of the basic barium salt (by means of barium hydroxide), and then in the form of the normal barium salt (by means of barium carbonate). The latter is purified by repeated resolution in water and precipitation from aqueous solution by alcohol. S. B. S.

Carnaubon, a Glycerol-free Phosphatide Containing Galactose. EDWARD K. DUNHAM and C. A. JACOBSON (*Zeitsch. physiol. Chem.*, 1910, **64**, 302—315).—This new phosphatide, $C_{74}H_{150}O_{13}N_3P$, prepared from ox-kidney, is soluble in alcohol and almost insoluble in ether. It is a triazomonophosphatide, is free from glycerol, and yields on cleavage, galactose (or amino-galactose), carnaubic, stearic, palmitic, and phosphoric acids and choline. Its constitution appears to be like that of lecithin, the sugar taking the place of glycerol; this allows of more acid groups being united with the molecule. There are probably other similar phosphatides differing in the nature of the sugar and acid groups. W. D. H.

The Simplest Fat, Glyceryl Triformate. PIETER VAN ROMBURGH (*Zeitsch. physikal. Chem.*, 1910, **70**, 459—461).—Glyceryl triformate has been obtained pure for the first time by the following method. Glycerol was heated repeatedly with 100% formic acid, the excess of acid being distilled off until a mixture rich in the triformin was obtained. The mixture was then cooled in liquid ammonia until a small crystal of the triformin was obtained; on then warming slowly up to 0°, with stirring, the triformin was obtained in colourless crystals, m. p. 18°; $D^{18} = 1.320$ (fused ester); $n_D^{18} = 1.4412$.

When rapidly heated, the pure ester distils almost unchanged at 266° (762 mm.). When heated very slowly, slight decomposition occurs at 210°. When traces of the lower esters are present, triformin decomposes on heating. It is practically insoluble in, and only slowly hydrolysed by, cold water; it is soluble and fairly rapidly hydrolysed in hot water. It is acted on normally by ammonia and aliphatic amines. G. S.

Preparation of Salts of Dibromobehenic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 215007, 215008, and 215009. Compare Abstr., 1908, i, 122).—The lead and barium salts of dibromobehenic acid have been previously described. *Calcium dibromobehenate* can be prepared (1) by saturating an alcoholic solution of calcium chloride with dry ammonia, filtering from precipitated ammonium chloride, and treating with a solution of dibromobehenic acid in the same solvent; (2) decomposing a very dilute aqueous solution of potassium behenate with calcium chloride; (3) shaking dibromobehenic acid during several days with a saturated solution of calcium hydroxide. It is a colourless, tasteless, odourless powder,

insoluble in water or alcohol, and as a therapeutic agent compares favourably with potassium bromide. *Strontium dibromobehenate* and *magnesium dibromobehenate* are analogously prepared as colourless, tasteless powders, insoluble in water or alcohol. F. M. G. M.

Structure of the Acids of Drying Oils. G. L. GOLDSOBEL (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 55—57).—The structure, $CH_3\cdot[CH_2]_4\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$, previously given by the author (*ibid.*, 1906, **38**, 182) for linoleic acid is confirmed by the optical properties of the acid, the second formula discussed, $CH_3\cdot[CH_2]_5\cdot CH:CH\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$, requiring higher molecular refraction and dispersion than those actually found.

Oxidation of the initial products of oxidation of linolenic and *iso*linolenic acids, namely, linusic and *iso*linusic acids, by means of permanganate yields in both cases (1) azelaic acid in almost quantitative amounts, and (2) propionic acid, which forms the principal product of the reaction. Consequently, linusic and *iso*linusic acids have the formula:

$$OH\cdot CHEt\cdot CH(OH)(C_4H_8O_2)\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

and linolenic and *iso*linolenic acids the formula:

$$CHEt:CH(C_4H_6)\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H.$$

As the presence of an allenic linking is excluded, the formula for linolenic and *iso*linolenic acids must be one of the three following:

(1) $CHEt:CH\cdot CH_2\cdot CH_2\cdot CH:CH\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$;
(2) $CHEt:CH\cdot CH_2\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$;
(3) $CHEt:CH\cdot CH:CH\cdot CH_2\cdot CH_2\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H$.

The optical data show that (2) is the correct formula; this result is confirmed by the observations of Erdmann, Bedford, and Raspe (Abstr., 1909, i, 358). T. H. P.

Oxidation of Methyl Ricinoleate by Ozone. ALBIN HALLER and ANDRÉ BROCHET (*Compt. rend.*, 1910, **150**, 496—503).—When methyl ricinoleate containing one-tenth of its weight of water is treated with ozone, it forms an *ozonide*, m. p. 80—85°, having the constitution:

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot\underbrace{CH\cdot CH}_{O_3}\cdot[CH_2]_7\cdot \underset{\underset{O}{\|}}{C}O\cdot OMe.$$

An examination of the decomposition products of this substance has established the constitution usually assigned to ricinoleic acid. When added to aqueous sodium carbonate solution the mixture separates into two layers. When acidified, the aqueous layer yields a mixture in which azelaic acid with its monomethyl ester and *β-hydroxynonoic acid*, $CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CO_2H$, have been identified. The latter has been isolated as brilliant lamellæ, m. p. 47—48°, showing $[\alpha]_D$ 2°26′ in alkaline solution. The *silver* salt is crystalline. The optically inactive acid, m. p. 61°, has been prepared by the action of heptaldehyde on the magnesium derivative of ethyl bromoacetate.

In an attempt to separate the above mixture of acids by distillation at 15 mm., Δ^{α}-*nonenoic acid* was obtained, but not in the pure state.

Those portions of the decomposition products which remained insoluble in alkali were found to contain (1) the *methyl* ester of *azelaic*

semi-aldehyde, $CHO\cdot[CH_2]_7\cdot CO_2Me$, which was isolated by means of its *bisulphite* compound and obtained as a liquid, b. p. 140—145°/15 mm. (compare Harries, Abstr., 1906, i, 11; Molinari, *ibid.*, 792). (2) A brown liquid, possibly having the composition

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CHO,$$

since on oxidation it furnished heptoic acid. (3) Methyl stearate and palmitate, together with oily substances of unknown composition.

W. O. W.

Preparation of Calcium Antimony Lactate. CHEMISCHE WERKE SCHUSTER & WILHEMY (D.R.-P. 216158).—Calcium antimony lactate was previously prepared by treating freshly precipitated antimony oxide with a solution of calcium hydrogen lactate, or a mixture of free lactic acid and calcium lactate. The double salt, $Sb(C_3H_5O_3)_3,Ca(C_3H_5O_3)_2$, can be readily prepared by treating an aqueous solution of antimony fluoride with the requisite amount of normal calcium lactate dissolved in a saturated solution of calcium sulphate, the presence of which is necessary to induce the reaction to take place.

F. M. G. M.

Conductivity Measurements with Dibasic Unsaturated Structure-isomeric Acids. FRITZ FICHTER and HANS PROBST (*Annalen*, 1910, **372**, 69—79. Compare Fichter and Müller, Abstr., 1906, i, 622).—The dissociation constants of four isomeric unsaturated dicarboxylic acids having the formula $C_7H_{10}O_4$ have been measured with the object of ascertaining the effect of the position of the ethenoid linking on the strength of the acid. The acids measured and the dissociation constants at 25° are: allylsuccinic acid, $CH_2{:}CH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0\cdot0109$; propenylsuccinic acid, $CHMe{:}CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0\cdot00596$; ethylitaconic acid, $CHEt{:}C(CO_2H)\cdot CH_2\cdot CO_2H$, $K=0\cdot00356$, and ethylmesaconic acid, $CH_2Et\cdot C(CO_2H){:}CH\cdot CO_2H$, $K=0\cdot093$. As usual, the highest value is obtained when the ethenoid linking is situated between the carboxyl groups; in the remaining cases, the strength of the acid increases as the ethylene linking becomes further removed from the carboxyl groups. This relationship does not always exist, however, for Stobbe has shown (Abstr., 1902, i, 461) that γ-ethylidene-γ-methylpyruvic acid, $CHMe{:}CMe\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, is a weaker acid than methylethylitaconic acid, $CMeEt{:}C(CO_2H)\cdot CH_2\cdot CO_2H$.

Propenylsuccinic acid was prepared by boiling the isomeric ethylitaconic acid with aqueous sodium hydroxide; it crystallises in large, colourless, transparent, crystals, m. p. 135°; the *calcium* salt, $C_7H_8O_4Ca$, is crystalline. An attempt to prepare it by distilling γ-methylparaconic-α-acetic acid led to the production of methylethylmaleic anhydride.

γ-Methylparaconic-α-acetic acid,

$$CHMe<\begin{matrix}CH(CO_2H)\\O\text{——}CO\end{matrix}>CH\cdot CH_2\cdot CO_2H,$$

prepared by reducing ethyl α-acetotricarballylate in alcoholic solution with sodium amalgam, is a crystalline powder, m. p. 175°; the *ethyl* ester, $C_{12}H_{18}O_6$, is a viscid oil, b. p. 198°/13 mm. W. H. G.

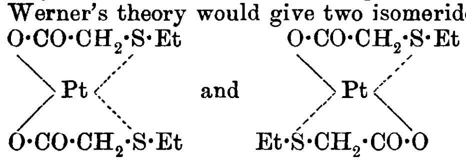
Molybdo-tartrates. P. QUINET (*Bull. Soc. chim.*, 1910, [iv], 7, 105).—The author points out in connexion with Grossmann's claim for priority on this subject (*ibid.*, December 5th, 1909) that his own work (Abstr., 1908, i, 713) does not cover the same ground as that of Grossmann and Pötter (Abstr., 1904, ii, 153; 1906, ii, 211; 1906, i, 799). The erroneous composition assigned to the compound of tartaric acid with sodium molybdate, given in the author's paper (*loc. cit.*) and noted by Grossmann (*loc. cit.*), had already been corrected (*J. phys.*, April, 1909). T. A. H.

The Electrolytic Degradation of the Saccharic Acids from Mono- and Di-saccharides, and also of Certain Hydroxy-amino-acids. CARL NEUBERG, L. SCOTT, and SIEGBERT LACHMANN (*Biochem. Zeitsch.*, 1910, 24, 152—165).—The general scheme of degradation may be represented by the formulæ:

$$OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CH(OH)\cdot CO_2H \longrightarrow OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CHO.$$

In this way the successive degradation of glucoheptonic acid to formaldehyde may be carried out. The electrolysis of the following acids is described: *d*-galactonic acid, *d*-*l*-erythronic acid, *d*-*l*-glyceric acid, and glycollic acid. The products obtained were *d*-lyxose, *d*-*l*-glyceraldehyde, glycolaldehyde, and formaldehyde. *iso*Serine was also electrolysed. Aminoacetaldehyde was not directly isolated in this case, but the products of electrolysis on oxidation with mercuric chloride and sodium hydroxide yielded its oxidation product, pyrazine. Melibionic acid, which was obtained in the form of the calcium salt, was also submitted to electrolysis. A sugar was obtained only in small quantity, and isolated in the form of its *p*-nitrophenylosazone. In most cases the salts of the alkaline earths of the above acids were employed in the electrolysis experiments. S. B. S.

Photo-transformation of an Internal Complex Salt. LUDWIG RAMBERG (*Ber.*, 1910, 43, 580—584).—Cryoscopic measurements show that platinous ethylthiolacetate (Abstr., 1906, i, 791) is slightly polymerised in aqueous solution. On exposure to sunlight, or to the rays from a Uviol lamp, the aqueous solution, which is slightly yellowish-green, gradually deepens in colour, and after a few days deposits canary-yellow, anhydrous needles or prisms, having the formula $Pt(CO_2\cdot CH_2\cdot SEt)_2$. They have m. p. 204—205°, and possess the normal molecular weight in glacial acetic acid solution, so that they are isomeric with the original compound of m. p. 189—190°. Werner's theory would give two isomerides having the configurations:



T. S. P.

Bimolecular Polymeride of Crotonaldehyde and the Corresponding Acid. MARCEL DELÉPINE (*Compt. rend.*, 1910, 150, 394—396. Compare Abstr., 1909, i, 84).—The compound $C_8H_{12}O_2$, formed in small quantity during the preparation of crotonaldehyde by the method already described, may be prepared in larger quantities by

heating in a reflux apparatus for half an hour a mixture of crotonaldehyde with the same weight of hydrochloric acid (D 1·18) and five times its weight of water. The liquid is then distilled. The new aldehyde forms an *azine*, $C_{16}H_{24}O_2N_2$, crystallising in sulphur-yellow prisms, m. p. 168°. On treatment with silver oxide (Abstr., 1909, i, 632) it yields the corresponding *acid*, $C_8H_{12}O_3,H_2O$, m. p. 68—71°. The anhydrous acid, obtained by heating at 60°, has m. p. 85—87°, b. p. 262—264°. The *ethyl* ester has b. p. 107—109°/18 mm., D_4^{20} 1·014, n_D 1·46102. Addition of bromine to an aqueous solution of the acid results in the formation of a *bromohydroxy-acid*, $C_8H_{13}O_4Br$, which crystallises in monoclinic prisms and does not lose water at 100°.
W. O. W.

Constitution of the Bimolecular Polymeride of Crotonaldehyde. MARCEL DELÉPINE (*Compt. rend.*, 1910, **150**, 535—537. Compare preceding abstract).—The polymeride obtained during the preparation of crotonaldehyde probably has the constitution

$$\begin{array}{l} CH_2\text{—}CH{:}C\cdot CHO \\ \vert \qquad\qquad \vert \\ CHMe\cdot O\cdot CHMe \end{array},$$

since on oxidation with chromic acid it forms acetic acid and carbon dioxide, and on treatment with magnesium ethyl bromide yields an *alcohol*, $C_7H_{11}O\cdot CHEt\cdot OH$, having a mint-like odour and forming a *monoacetyl* derivative. The *compound*, $C_7H_{11}O\cdot CH{:}CHMe$, has also been obtained as an agreeably-smelling liquid with a sweet taste, b. p. 82—84°/18 mm.; D_4^0 0·92061; n_D^{20} 1·48567. The ethyl ester of the acid corresponding with the above aldehyde furnishes, on treatment with magnesium ethyl iodide, a *compound*, $C_{12}H_{22}O_2$; this is probably a tertiary alcohol; it has an odour resembling that of pinacone, and does not form an acetyl derivative; b. p. 260°/760 mm., 151—154°/19 mm.; D_4^0 0·9731; n_D^{20} 1·46291.

Refractometric determinations are in agreement with the constitution suggested for the aldehyde. Crotonaldehyde has n_D^{10} 1·44361.
W. O. W.

Alkylation of Aliphatic Ketones by the Use of Sodamide. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1910, **150**, 582—589. Compare Abstr., 1904, i, 600; 1905, i, 276; 1909, i, 987).—Pinacolin is readily attacked in ethereal solution by sodamide, forming a soluble sodium derivative, which, on treatment with alkyl iodides, gives rise to a mixture of mono- and di-alkylpinacolins; these can be separated by fractional distillation. Trialkylpinacolins are not produced unless the reaction is carried out in presence of benzene or toluene, when the yield is practically quantitative. The ketones prepared in this way have been reduced to the corresponding secondary alcohols by means of sodium and absolute alcohol. Whilst the mono- and di-alkylpinacolins form oximes and semicarbazones, the trialkyl derivatives do not react with hydroxylamine or semicarbazide. The following compounds are described: the *oxime* of $\beta\beta$-dimethylpentan-γ-one crystallises in lozenges, m. p. 78—80° (compare Wischnegradsky, *Annalen*, 1875, **178**, 104). Nef's *iso*propyl butyl ketone (Abstr., 1900, i, 349) has D_4^2 0·80536, n_D 1·40513, and on reduction yields

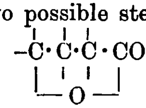
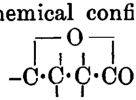
ββδ-trimethylpentan-γ-ol, $CMe_3{\cdot}CH(OH){\cdot}CHMe_2$, a liquid having an odour like borneol, b. p. 145—148°; the *phenylurethane* has m. p. 79°.

ββδδ-Tetramethylpentan-γ-one, $CMe_3{\cdot}CO{\cdot}CMe_3$, obtained by the action of sodamide on the foregoing ketone, has a camphoraceous odour, b. p. 149—151°, D_4^{25} 0·81992, n_D 1·41702. *ββδδ-Tetramethylpentan-γ-ol*, $CH(OH)(CMe_3)_2$, m. p. 50°, b. p. 165—166°, forms a *phenylurethane*, m. p. 118—119°; the *formyl* derivative has b. p. 185°. *ββδδ-Tetramethylhexan-γ-one*, $CMe_3{\cdot}CO{\cdot}CMe_2Et$, b. p. 172—174°; *ββδδ-tetramethylhexan-γ-ol*, b. p. 187—188°; its *phenylurethane* has m. p. 94—95°. *ββ-Dimethylhexan-γ-one*, $CMe_3{\cdot}CO{\cdot}Pr^a$, b. p. 146—148°, D_4^{25} 0·81055, n_D 1·40952; the *oxime* has m. p. 76—77°. *ββ-Dimethylhexan-γ-ol*, b. p. 155—157°, forms a *phenylurethane*, m. p. 70—71°. *ββ-Dimethyl-δ-ethylhexan-γ-one*, $CMe_3{\cdot}CO{\cdot}CHEt_2$, has b. p. 174—176°, D_4^{25} 0·82521, n_D 1·42227, and on reduction yields *ββ-dimethyl-δ-ethylhexan-γ-ol*, $CMe_3{\cdot}CH(OH){\cdot}CHEt_2$, b. p. 187°; the *phenylurethane* has m. p. 107°. *ββ-Dimethyl-δδ-diethylhexan-γ-one*; $CMe_3{\cdot}CO{\cdot}CEt_3$, b. p. 214—216°; *ββ-dimethyl-δδ-diethylhexan-γ-ol*, b. p. 226—228°, gives a *phenylurethane*, m. p. 110°. *ββδ-Trimethylhexan-γ-one*,

$CMe_3{\cdot}CO{\cdot}CHMeEt$,

b. p. 155—156°; *ββδ-trimethylhexan-γ-ol*, $CMe_3{\cdot}CH(OH){\cdot}CHMeEt$, b. p. 169°; the *phenylurethane* has m. p. 78°. *ββε*-Trimethylhexan-γ-one, $CMe_3{\cdot}CO{\cdot}CH_2Pr^\beta$, b. p. 157·5—158·5°, forms an oxime, m. p. 77—78° (compare Nef, Abstr., 1902, i, 6). *ββ-Dimethyl-Δ^ζ-hepten-γ-one*, $CMe_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$, b. p. 61—64°/14 mm. *ββ-Dimethyl-δ-allyl-Δ^ζ-hepten-γ-one*, $CMe_3{\cdot}CO{\cdot}CH(C_3H_5)_2$, b. p. 83—86°/14 mm.

W. O. W.

Relation between the Chemical Constitution and the Optical Rotatory Power of the Sugar Lactones. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1910, **32**, 338—346).—Data are quoted which show that the aldose sugars and their glucosidic and lactonic derivatives exhibit strong optical rotatory power, whilst the corresponding alcohols and acids have but slight optical activity. It is therefore evident that the lactonic structure causes considerable rotatory power. There are two possible stereochemical configurations for the lactonic ring, namely,  and . If the rotation is due to this ring, the sign of the rotation must be determined by the position of the ring. This position is determined by the position of the hydroxyl group attached to the γ-carbon atom before the ring was produced. The hypothesis is advanced that dextrorotatory lactones have the lactonic ring on one side of the structure, lævorotatory lactones have it on the other side, and the position of the ring shows the position in which the hydroxyl group was attached to the γ-carbon atom. A list is given of all the sugar lactones of which the structure and specific rotation have been determined, and it is shown that, in all cases, the theory is confirmed.

Suggestions are made with reference to the application of this theory to the determination of the constitution of the sugars.

E. G.

Behaviour of the Ordinary Hexoses towards Hydrogen Peroxide in Presence of Alkali Hydroxides as well as of Various Iron Salts. H. A. SPOEHR (*Amer. Chem. J.*, 1910, **43**, 227—254).—It has been shown by Nef (Abstr., 1908, i, 5) that when the hexoses are oxidised by air or mercuric oxide in presence of alkali hydroxide or by Fehling's solution, the same oxidation products are formed in each case and in the same proportions. A study has now been made of the oxidation of dextrose, lævulose, and galactose by hydrogen peroxide in presence of alkali hydroxide. It has been found that instead of the various products being obtained which are formed when the oxidation is effected in alkaline solution by means of air, Fehling's solution, or mercuric oxide, the only oxidation products obtained with dextrose and lævulose are formic acid, carbon dioxide, glycollic acid, and α-hydroxymethyl-*d*-arabonic acid, whilst with galactose, formic acid, carbon dioxide, glycollic acid, and α-hydroxymethyl-*d*-lyxonic acid are produced. The amount of formic acid obtained varied from 48·3 to 65·3% of the calculated amount possible in the case of dextrose and lævulose, and was over 80% in the case of galactose. From these results it follows that the only sugars present in the alkaline solutions which are actually selectively oxidised are (1) formaldehyde; (2) glycollaldehyde, which is converted partly into glycollic acid, and partly through glyoxylic acid into carbon dioxide and formic acid; (3) α- and β-*d*-glutose (from dextrose and lævulose), $OH\cdot CH_2\cdot \underset{H}{\overset{OH}{C}}\text{-}CO\text{-}\underset{H}{\overset{OH}{C}}\text{—}\underset{H}{\overset{OH}{C}}\cdot CH_2\cdot OH$ and

$$OH\cdot CH_2\cdot \underset{OH}{\overset{H}{C}}\text{-}CO\text{-}\underset{H}{\overset{OH}{C}}\text{—}\underset{H}{\overset{OH}{C}}\cdot CH_2\cdot OH,$$

which give the same glutosone, $OH\cdot CH_2\cdot CO\cdot CO\cdot \underset{H}{\overset{OH}{C}}\text{—}\underset{H}{\overset{OH}{C}}\cdot CH_2\cdot OH,$ this yielding only α-hydroxymethyl-*d*-arabonic acid,

$$CO_2H\cdot \underset{OH}{\overset{CH_2\cdot OH}{C}}\text{———}\underset{H}{\overset{OH}{C}}\text{—}\underset{H}{\overset{OH}{C}}\cdot CH_2\cdot OH;$$

or α- and β-galtose (from galactose), which similarly yield α-hydroxymethyl-*d*-lyxonic acid, $CO_2H\cdot \underset{OH}{\overset{CH_2\cdot OH}{C}}\text{———}\underset{OH}{\overset{H}{C}}\text{—}\underset{H}{\overset{OH}{C}}\cdot CH_2\cdot OH.$

*α-Hydroxymethyl-*d*-arabonic lactone*, $[\alpha]_D$ +72·5°, is a viscous substance. The *phenylhydrazide*, $C_6H_{11}O_6\cdot NH\cdot NHPh$, m. p. 212—215°, forms lustrous needles. The *brucine* salt, m. p. 186—188°, $[\alpha]_D^{20}$ about −25·7°, and the *calcium* salt, $[\alpha]_D$ about −3·0°, are described.

*Brucine α-hydroxymethyl-*d*-lyxonate*, m. p. 171—175°, the corresponding *quinine* salt, m. p. 213°, and the *phenylhydrazide*, m. p. 144°, are described.

Experiments have shown that ethylene glycol and glycollic acid,

when oxidised by an alkaline solution of hydrogen peroxide, yield small quantities of formic and carbonic acids, but no oxalic acid.

Morrell and Crofts (Trans., 1899, **75**, 786; 1902, **81**, 666; 1903, **83**, 1290) have studied the oxidation of dextrose, lævulose, and galactose with hydrogen peroxide in presence of ferrous sulphate, and have obtained the hexosone, and glycollic, glyoxylic, and oxalic acids as the oxidation products. These authors have also stated that erythronic (trihydroxybutyric) acid is formed from dextrose and lævulose. On repeating these experiments, erythronic acid could not be obtained, but it is regarded as probable that a ketonic acid or a mixture of ketonic acids containing four carbon atoms is produced. Formic, carbonic, and oxalic acids were isolated. It is considered that the large quantity of oxalic acid (18—27%) produced is due to a direct hydrolysis of polyhexosones, such as $\mathrm{CHO\cdot CO\cdot CO\cdot}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{—}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{\cdot CH_2OH}$ and $\mathrm{CHO\cdot CO\cdot CO\cdot CO\cdot}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{\cdot CH_2OH}$, formed as the first products of the oxidation. E. G.

Mechanism of the Oxidation of Dextrose by Bromine. HERBERT H. BUNZEL (*J. Biol. Chem.*, 1910, **7**, 157—169. Compare Bunzel and Mathews, Abstr., 1909, i, 289).—Experiments have been made on the oxidation of dextrose with bromine in the presence of dilute sulphuric acid ($0{\cdot}1N$). The equation used for calculating K was $K = 1/t(a-x)\log.\mathrm{nat}.b(a-x)/a(b-x)$, where a and b are the respective concentrations of the active bromine and sugar at the start, and x the amount of sugar and bromine used up during the time t. This equation gave constant values for K when sodium bromide was added, so that the concentration of the $\overline{\mathrm{Br}}$ ions was $0{\cdot}3N$ in the final mixture; as the bromine in these experiments was only $0{\cdot}01N$, the slight increase in the concentration of the $\overline{\mathrm{Br}}$ ions during the reaction was negligible. When no sodium bromide was added, K was calculated from the equation:

$$K = \frac{1}{t\dfrac{0{\cdot}05\,(a-b)}{0{\cdot}5 + \mathrm{Br}\ (\text{at start}) + \dfrac{\mathrm{HBr}t_2 - \mathrm{HBr}t_1}{2} - \mathrm{Br}_3}(a-b)}\log\frac{b(a-x)}{a(b-x)}.$$

Titrations of the acid formed during the reaction indicate that for each molecule of bromine used up a molecule of gluconic acid is formed. Of the total acidity produced during the reaction, it was shown that two-thirds are due to hydrobromic acid and one-third to organic acid (gluconic acid).

The results agree with the view expressed previously, that dextrose in aqueous solution can ionise in two different ways. J. J. S.

The Contraction Occurring when Sucrose is Dissolved in Water and the Density of Sucrose. A. DÉMICHEL (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 753—755. Compare Abstr., 1909, ii, 795 ; this vol., i, 96).—The author calculates the density of sucrose to be 1·581, using for this purpose the tables published by Buisson, and he shows that the contraction taking place when sucrose is dissolved in water may be calculated when the densities of the sucrose, of the water, of the sucrose solution, and the amount of sucrose in the latter, are known. He shows that there is always a contraction and never an expansion. W. P. S.

Contraction Occurring during Solution and the Law of Guéritsch. A. DÉMICHEL (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 755—757).—The contraction taking place when sucrose is dissolved may be measured by differences in density, but the author considers that it is more rational to express the contraction as a difference in volume, and gives formulæ for thus calculating the contraction. The law of Guéritsch only allows a more or less imperfect approximation of the contraction to be obtained even in cases where the concentration is such that the phenomenon is most appreciable. W. P. S.

Change of Rotation of Sucrose in Presence of Alkaline Uranyl Salt Solutions. HERMANN GROSSMANN and F. ROTHGIESSER (*Ber.*, 1910, **43**, 676—682. Compare Abstr., 1906, ii, 61).—Sucrose is slowly changed into lævorotatory compounds by the action of uranyl nitrate and sodium hydroxide. Variations in the relative proportions and concentration of sucrose, uranyl nitrate, and alkali are of the greatest influence on the character of the change and on the end point of the reaction. Using 1 mol. of sucrose to 1 mol. of nitrate, the initial rotation is twice that of sucrose ; it falls gradually to a negative value. With 2 mols. of nitrate and 15 mols. of sodium hydroxide to 1 mol. of sucrose, the initial rotation is nil, and the final reading $-126·7°$. The change is due to the slow hydrolysis of the many complex salts in solution in accordance with the scheme :

$$C_{12}H_{20}O_9(O\cdot UrO_2\cdot ONa)_2 + 2H_2O \rightleftarrows C_{12}H_{20}O_9(O\cdot UrO_2\cdot OH)_2 + 2NaOH$$
$$C_{12}H_{21}O_{10}(O\cdot UrO_2\cdot ONa) + H_2O \rightleftarrows C_{12}H_{21}O_{10}(O\cdot UrO_2\cdot OH) + NaOH.$$

The complex salts are probably strongly dextrorotatory but their products of hydrolysis are highly lævorotatory. Hence an increase in the amount of water displaces equilibrium in favour of the right-hand equation, whilst concentrated sodium hydroxide favours the reverse change. E. F. A.

Configuration of Rhodeose. EMIL VOTOČEK (*Ber.*, 1910, **43**, 469—475).—Polemical. Rhodeose is the mirror image of fucose, and the configuration is established by the behaviour of rhodeitol towards sorbose bacteria and by the oxidation of rhodeonic acid to *l*-trihydroxyglutaric acid (Votoček, Abstr., 1906, i, 378, 483). The configuration of fucose was accordingly established in 1906 (compare Mayer and Tollens, Abstr., 1907, i, 588). E. F. A.

Additive Products of Hydrogen Cyanide with Rhodeose. CYRILL KRAUTZ (*Ber.*, 1910, **43**, 482—488. Compare Votoček, preceding abstract).—By the addition of hydrogen cyanide to rhodeose and hydrolysis, two isomeric rhodeohexonamides are formed: the α-isomeride forms large, colourless prisms, m. p. 206°; the β-isomeride is amorphous, m. p. 197—198°. On hydrolysis with barium hydroxide the *barium* salts of the isomeric rhodeohexonic acids are obtained; that from the α-amide has $[\alpha]_D^{20}$ + 6·88°, and from the β-amide, $[\alpha]_D^{20}$ − 1·49°. α-*Rhodeohexonic acid* is rapidly converted into the lactone, and shows $[\alpha]_D^{20}$ − 30·25° in solution. The salts are amorphous and deliquescent, with the exception of the *barium* and *lead* compounds. β-*Rhodeohexonic acid* gives $[\alpha]_D^{20}$ − 44·25° in solution; the salts are similar to those of the α-isomeride. The *lactone* of the α-acid separates in large, well-formed prisms of sweet taste and neutral reaction, m. p. 129—131°, $[\alpha]_D^{20}$ − 34·8°. The *lactone* of the β-acid reacts faintly acid, tastes sweet, m. p. 115°, $[\alpha]_D^{20}$ − 40·6°. The α-*phenylhydrazide* crystallises in lustrous, silver plates, m. p. 231° (decomp.); the β-*phenylhydrazide* is a glistening, yellow compound, m. p. 211° (decomp.).

The lactones on reduction with sodium amalgam in faintly acid solution at − 5° form the corresponding rhodeohexoses. α-*Rhodeohexose* is a microcrystalline substance, m. p. 125—126°, $[\alpha]_D^{20}$ + 11·96°; β-*rhodeohexose* is amorphous.

The following derivatives were prepared by the usual methods from α-rhodeohexose: The *phenylhydrazone* forms yellow plates, m. p. 150°; the p-*bromophenylhydrazone* is a colourless powder, m. p. 173°; the *phenylmethylhydrazone* forms colourless plates, m. p. 188°; the *phenylosazone* separates in golden-yellow needles, m. p. 231°; the p-*bromophenylosazone* is similar, m. p. 219°.

Of β-rhodeohexose, the *phenylhydrazone* crystallises in colourless plates, m. p. 131—137°; the p-*bromophenylhydrazone* is colourless, m. p. 145°; the *phenylmethylhydrazone* forms silvery, glistening tablets, m. p. 163°; the *phenylosazone* is a citron-yellow powder, m. p. 213°; the p-*bromophenylosazone* is an orange-yellow powder, m. p. 200°.

α- and β-Rhodeohexone lactones are mutually interconvertible when heated in aqueous solution with pyridine at 150°. E. F. A

Acetylation of Cotton Cellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1910, **23**, 433—441).—A résumé of the different methods of acetylation of cellulose is given. Mork, Little and Walker (Amer. Pat., 709922) use aromatic sulphonic acids instead of mineral acids as catalysts. The author's experiments point to the fact that phenolsulphonic acid acts as a catalyst in the acetylation of cellulose, owing to the fact that free sulphuric acid is formed during the reaction. The addition of sodium phenolsulphonate to the mixture does not get rid of the free sulphuric acid, as the reaction between the sodium salt and sulphuric acid is slow. In commercial specimens of phenolsulphonic acid appreciable amounts of sulphuric acid are always present, but even when the pure sulphonic acid is used with pure acetic anhydride and cellulose, the presence of sulphuric acid can be detected after some little time. If barium phenolsulphonate is added to the mixture, the acetylation requires a much longer time, owing to the removal of

most of the sulphuric acid as insoluble barium sulphate. The addition of sulphates, for example, ferrous sulphate, dimethylamine sulphate, and sulphates derived from feeble bases, to acetic anhydride has also been recommended, and in these cases, also, the catalytic action is due to the liberation of small amounts of free sulphuric acid.

Various specimens of acetylcellulose have been prepared by Bayer's method (D.R.-P. 159524) and by Lederer's method (D.R.-P. 163316). The products have been hydrolysed by 25% aqueous potassium hydroxide solution at the ordinary temperature during forty-eight hours, and the reducing powers of the products of hydrolysis determined by means of boiling alkaline copper solution. After allowing for the reducing properties of the original cellulose and of the hydrated cellulose formed by the action of acids and alkalis on the cellulose (Normann, Abstr., 1906, i, 560), a mean copper value of four was obtained. This is due to the formation of hydrocelluloses, and the conclusion is drawn that the processes of Bayer and of Lederer are identical as regards their chemical mechanism. J. J. S.

Fixation of Bases by Soluble Starch. EUGÈNE FOUARD (*Bull. Soc. chim. Belg.*, 1910, **24**, 105—109).—It is pointed out that there is no actual difference between the author's interpretation of his results (Abstr., 1909, i, 13, 209, 699) and that given by Reychler (Abstr., 1909, ii, 977). The action of bases appears to be to disintegrate the complex starch molecules with the formation of a simple group $(C_6H_{10}O_5)'$, which then reacts with the base, so that in the reversible reaction disintegration and re-formation of complex molecules occur. T. A. H.

Stachyose. CARL NEUBERG and SIEGBERT LACHMANN (*Biochem. Zeitsch.*, 1910, **24**, 171—177).—Stachyose is only attacked very slowly by emulsin. It readily undergoes hydrolysis, however, when treated with yeast maltase and kephir lactase, yielding lævulose and mannino-triose. The last-named trisaccharide was obtained in the form of its osazone, which melts at 192—194°, and not at 122°, the melting point given by Tanret for the mannotrisaccharideosazone prepared by him from stachyose. The authors also give their method of preparation of stachyose from the bulbs of *Stachys tubifera*. S. B. S.

New Compound Contained in Foods. A. BACKE (*Compt. rend.*, 1910, **150**, 540—543).—Baked bread and biscuits contain traces of a crystalline *compound*, m. p. 95°, which resembles in some respects Brandt's maltol, and shows many of the reactions of salicylic acid. It differs from the latter in its behaviour in Zipper's and Jorrisen's reactions, and in undergoing decomposition when heated with sodium hydroxide. With traces of ferric chloride, it develops a red coloration, becoming violet on adding a larger quantity of the reagent. The substance is isolated by treating bread with sulphuric or phosphoric acid, distilling in steam, and extracting the distillate with ether. It appears to be formed, together with maltol, when many sugars and starchy materials are acted on by an unknown enzyme and then heated at 120—150°. The enzyme necessary to its formation occurs together with amylase in flour and malt. W. O. W.

Preparation of Choline and Some of its Salts. ROEMER R. RENSHAW (*J. Amer. Chem. Soc.*, 1910, **32**, 128—130).—Choline hydrochloride can be obtained in nearly quantitative yield by passing a current of dry trimethylamine into freshly distilled anhydrous ethylene chlorohydrin at $-12°$ to $-20°$ contained in a tube, which is afterwards sealed and heated for two hours at 80—90°. The salt can be purified by adding ether to an alcoholic solution. Choline *acetate*, *sulphate*, and *dihydrogen phosphate* are described. E. G.

Derivatives of Amino-acids. I. Compounds with Glycerol. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 53—60).—The authors have attempted to prepare derivatives of amino-acids with various aliphatic and aromatic compounds, including glycerol, in order to examine the behaviour of such compounds under the conditions which exist in the complete hydrolysis of proteins.

It has not been found possible to condense glycine or tyrosine with glycerol in the presence of dry hydrogen chloride at 185°, or glycerolsulphuric acid with glycine at 100°. Silver glycine and silver alanine do not react with the monohalohydrins of glycerol. Glycerolsulphuric acid, however, condenses with halogenated acyl chlorides.

*Bisbromo*iso*valerylglycerol*, $OH{\cdot}CH(CH_2{\cdot}O{\cdot}CO{\cdot}C_4H_9Br)_2$, obtained from bromo*iso*valeric acid, sulphuric acid, and glycerol at 70—80° (compare Grün, Abstr., 1905, i, 562; 1907, i, 462, 464), is a thin, colourless oil with a bitter taste, b. p. 185—200°/0·3 mm. Treatment with aqueous, alcoholic or liquid ammonia leads to decomposition of the ester and formation of a halogenated acid amide.

Glycine chloride does not appear to react with the sodium derivatives of glycerol, or yet with dipalmitin, in the presence of chloroform, but bromo*iso*valeryl bromide reacts with dipalmitin at 100°, yielding *glyceryl bromo*iso*valerate dipalmitate*,

$$C_{10}H_9Br{\cdot}CO{\cdot}O{\cdot}CH(CH_2{\cdot}O{\cdot}CO{\cdot}C_{15}H_{31})_2,$$

which crystallises in microscopic needles; it melts at 51° to a turbid liquid, which clarifies at 60°.

Tyrosine derivatives of glycerol are readily prepared, but are very sparingly soluble and difficult to purify.

Glycerolmonotyrosine,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

obtained by the action of glyceryl-α-monochlorohydrin on freshly prepared sodium tyrosinate, forms colourless needles, m. p. 245° (uncorr., decomp.), and is optically inactive. It is not hydrolysed when boiled for six hours with fuming hydrochloric acid. J. J. S.

Derivatives of Amino-acids. II. Compounds with Aliphatic Acids. EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1910, **65**, 61—68. Compare Bondi, Abstr., 1909, i, 458; Bondi and Frankl, *ibid.*, 459).—The authors object to the name lipopeptide for the condensation products of acyl chlorides with amino-acids; the name should be reserved for compounds containing a free amino-group.

Palmitylglycine, $CH_3{\cdot}[CH_2]_{14}{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, obtained by the

action of palmityl chloride on glycine in the presence of dilute sodium hydroxide solution, crystallises in slender needles, m. p. 125° (corr.), after sintering at 119°. The corresponding *ethyl* ester, $C_{20}H_{39}O_3N$, also crystallises in needles, has m. p. 80—85°, and on hydrolysis yields palmitylglycine.

Palmityl-d-*alanine*, $CH_3\cdot[CH_2]_{14}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, has m. p. 110°, after sintering at 105°, and $[\alpha]_D^{20}$ −5·98°.

Palmityl-l-*tyrosine*, $CH_3\cdot[CH_2]_{14}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH$, crystallises in plates, m. p. 133°, after sintering at 120°, and $[\alpha]_D^{20}$ +24·35°. *Palmityl*-l-*tyrosinyl palmitate*,

$$C_{15}H_{31}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot O\cdot CO\cdot C_{15}H_{31},$$

forms colourless needles, m. p. 95—96°, after sintering at 87°, $[\alpha]_D^{20}$ +15·28°.

Palmityl-3 : 5-*di-iodo*-l-*tyrosinyl palmitate*,

$$C_{15}H_{31}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2I_2\cdot O\cdot CO\cdot C_{15}H_{31},$$

forms microscopic needles, sinters at 50°, melts at 55°, and forms a clear liquid at 62°.

Stearylglycine, $C_{17}H_{35}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, crystallises in plates, m. p. 155°, after sintering at 145°. *Stearyl*-d-*alanine*,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

crystallises in needles, m. p. 105—108°, $[\alpha]_D^{20}$ −4·55°.

Stearyl-l-*tyrosinyl stearate*,

$$C_{17}H_{35}\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot O\cdot CO\cdot C_{17}H_{35},$$

forms slender needles, it sinters at 88°, melts at 98° to a turbid liquid, and becomes quite clear at 108°.

Palmityl-*dl*-phenylalanine, palmityl-*dl*-leucine, stearyl-*d*-glutamic acid, palmitylcystine, and palmityl-*l*-tryptophan have also been prepared.

It is difficult to obtain the tyrosine compounds in a state of purity.

J. J. S.

Synthesis of *dl*-Arginine (α-Amino-δ-guanino-*n*-valeric Acid) and of the Isomeric α-Guanino-δ-amino-*n*-valeric Acid. Sören P. L. Sörensen (*Ber.*, 1910, **43**, 643—651).—The proof that *d*-*l*-arginine is α-amino-δ-guanino-*n*-valeric acid has been established by condensing cyanamide with α-benzoylornithine to α-benzoylamino-δ-guanino-*n*-valeric acid and subsequent hydrolysis with hydrochloric acid, when a product identical with *d*-*l*-arginine is obtained.

The isomeric δ-amino-α-guanino-*n*-valeric acid can by obtained in a similar manner from δ-benzoylornithine.

A 75% yield of δ-benzoylornithine is obtained when ornithuric acid is boiled with hydrochloric acid, and a 52% yield of the isomeric *α-benzoylornithine*, $NH_2\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot COPh$, is obtained when ornithuric acid is boiled with barium hydroxide solution. The α-compound forms long, thin crystals, m. p. 264—267°, is some three to four times as soluble in water as the δ-compound, and does not crystallise so readily. The δ-compound (Fischer, *Ber.*, 1901, **34**, 463) has m. p. 285—288°. The constitution of the two benzoyl derivatives has been established by replacing the amino-groups by hydroxyl. α-Benzoylamino-δ-hydroxyvaleric acid (Abstr., 1908, i, 651) has m. p. 160° (not 170°). The *δ-benzoylamino-α-hydroxyvaleric acid*,

$$C_6H_5\cdot CO\cdot NH\cdot[CH_2]_3\cdot CH(OH)\cdot CO_2H,$$

is readily soluble in water, crystallises from benzene in needles, m. p. 85°, yields a sparingly soluble *barium* salt, and when hydrolysed yields Fischer and Zemplen's δ-amino-α-hydroxyvaleric acid (this vol., i, 100).

*α-Benzoylamino-δ-guanino-*n*-valeric acid*,

$NH_2\cdot C(:NH)\cdot NH\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot COPh$,

obtained, together with dicyanodiamide and barium carbonate, by leaving α-benzoylornithine and cyanamide in contact with 0·4*N*-barium hydroxide solution for a month, crystallises in well developed four- and six-sided plates, and also in stout prisms, m. p. 315° (decomp.).

*δ-Benzoylamino-α-guanino-*n*-valeric acid*,

$COPh\cdot NH\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot C(:NH)\cdot NH_2$,

obtained in a similar manner from δ-benzoylornithine, forms a curdy mass of minute needles containing $3H_2O$. When anhydrous it has m. p. 175—180°. J. J. S.

Synthesis of Glycylaminoacetaldehyde. CARL D. HARRIES and IRNFRIED PETERSEN (*Ber.*, 1910, **43**, 634—639).—Polypeptides obtained from amino-acids and amino-aldehydes are termed *peptals*, the simplest representative being *glycylaminoacetaldehyde*,

$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CHO$.

This aldehyde has been synthesised by the two following methods: 1. Glycylallylamine, obtained by the action of ammonia on the condensation product of allylamine and chloroacetyl chloride, is readily oxidised in the form of its hydrochloride to glycylaminoacetaldehyde by means of ozone (compare Harries and Richard, Abstr., 1904, i, 295). 2. Glycylaminoacetal, obtained by the action of ammonia on the condensation product of chloroacetyl chloride and aminoacetal, is hydrolysed by hydrochloric acid to glycylaminoacetaldehyde.

The aldehyde has so far not been obtained pure, but merely in the form of a syrup with strongly reducing properties.

Chloroacetylallylamine, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CH:CH_2$, is a colourless, syrupy liquid, b. p. 110—112°/14 mm., and solidifies in a freezing mixture; it has $D_{19.5}^{19.5}$ 1·1683 and $n_D^{19.5}$ 1·48917. *Glycylallylamine*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH:CH_2$, is a colourless oil, b. p. 85—91°/0·19 mm., D_{20}^{20} 1·0532, and n_D^{20} 1·49585. It absorbs carbon dioxide rapidly, and forms a *picrate*, $C_{11}H_{13}O_8N_5$, m. p. 136—138°. The *benzoyl* derivative, $C_{12}H_{14}O_2N_2$, crystallises in plates, m. p. 138°. If liquid ammonia is used instead of an aqueous solution for replacing the chlorine in chloroacetylallylamine, a by-product is obtained, which has b. p. 187°/0·19 mm.; it is probably *iminodiacetyldiallylamine*,

$NH(CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH:CH_2)_2$.

Chloroacetylaminoacetal, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, has b. p. 80—85°/0·14 mm., and solidifies to a colourless, crystalline mass, m. p. 29—30°.

Glycylaminoacetal, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, has b. p. 107—110°/0·14 mm. and m. p. 42—45°, and yields a colourless, crystalline hydrochloride, $C_8H_{18}O_3N_2,HCl$. The acetal is readily hydrolysed by cold dilute hydrochloric acid. J. J. S.

Preparation of Nitrogen Derivatives of Formaldehydesulphoxylic Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 216074).—The reduction of *sodium aminomethylsulphite*,

$$NH_2(CH_2{\cdot}O{\cdot}SO_2Na),$$

sodium iminodimethylsulphite, $NH(CH_2{\cdot}O{\cdot}SO_2Na)_2$, and of sodium nitrilotrimethylsulphite, $N(CH_2{\cdot}O{\cdot}SO_2Na)_3$, with zinc at 60—70° in either acid or ammonium hydroxide solution yields respectively *sodium aminomethylsulphoxylate*, $NH_2(CH_2{\cdot}O{\cdot}SONa)$, *sodium iminodimethylsulphoxylate*, $NH(CH_2{\cdot}O{\cdot}SONa)_2$, and *sodium nitrilotrimethylsulphoxylate*, $N(CH_2{\cdot}O{\cdot}SONa)_3$.

The relative proportion of indigotin reduced by these substances is stated in the patent. F. M. G. M.

Preparation of Nitrogen Derivatives of Aldehyde Bisulphites. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 216072).—*Sodium iminodimethylsulphite*, $NH(CH_2{\cdot}O{\cdot}SO_2Na)_2$, is prepared by treating a solution of ammonium hydroxide with two molecular proportions of formaldehyde bisulphite solution at 45° and evaporating under reduced pressure, when the product separates as a colourless powder, or as hard crystals. The ammonium hydroxide in the foregoing reaction can be replaced by other primary amines, the resulting products being powerful reducing agents. F. M. G. M.

Preparation of Nitrogen Derivatives of Aldehyde Bisulphites. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 216073. Compare preceding abstract).—*Sodium nitrilotrimethylsulphite*,

$$N(CH_2{\cdot}O{\cdot}SO_2Na)_3,3H_2O,$$

separates as prismatic crystals when a solution containing three molecular proportions of formaldehyde bisulphite and one of ammonia is concentrated under reduced pressure; it is readily soluble in water, sparingly so in alcohol, is decomposed by sodium hydroxide with evolution of ammonia, and by mineral acids with elimination of sulphurous acid. F. M. G. M.

Preparation of Nitrogen Derivatives of Formaldehydesulphoxylates. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 216121).—*Sodium nitrilotrimethylsulphoxylate*, $N(CH_2{\cdot}O{\cdot}SONa)_3$, can be prepared by reducing sodium nitrilotrimethylsulphite,

$$N(CH_2{\cdot}O{\cdot}SO_2Na)_3,$$

with zinc in either acid or ammonium hydroxide solution, and subsequently concentrating in a vacuum; it is a colourless, resinous mass, very readily soluble in water, insoluble in anhydrous solvents, and reduces indigo-carmine rapidly in the cold. The *zinc* salt is a powerful reducing agent; the *calcium* salt is somewhat sparingly soluble in sodium chloride solution. F. M. G. M.

ζ-Amino-ketones. II. SIEGMUND GABRIEL (*Ber.*, 1910, **43**, 356—362. Compare Abstr., 1909, i, 891).—Methyl ζ-aminohexyl ketone, the *benzenesulphonyl* derivative of which has m. p. 77—78°, is reduced by sodium and alcohol to η-hydroxyoctylamine, which forms a *hydrochloride*, $OH{\cdot}CHMe{\cdot}[CH_2]_6{\cdot}NH_2,HCl$, m. p. above 80°, a *platinichloride*, m. p. 201° (decomp.), and is converted by concentrated hydrochloric acid at 100° into *η-chloro-octylamine*, which forms a

platinichloride, darkening at 206°, and decomposing at 210°. A by-product of the reduction is a *substance*, $C_8H_{17}N$, which appears to be a saturated secondary base, and is possibly 2-methylheptamethylene-imine; it forms a *hydrochloride*, m. p. 148—149°, *platinichloride*, m. p. 153—155°, *aurichloride*, m. p. 67—68°, *picrate*, m. p. 152—153°, and a *benzenesulphonyl* derivative, $C_8H_{16}N\cdot SO_2Ph$, m. p. 114—115°, which is insoluble in alkalis. C. S.

Partial Inversion of Optical Antipodes. OSCAR LUTZ (*Zeitsch. physikal. Chem.*, 1910, **70**, 256—262).—In the course of his investigations on the Walden inversion, Fischer (compare Fischer and Raske, Abstr., 1907, i, 381) has shown that the occurrence of inversion depends on the nature of the substance acted on as well as on that of the reagent. The author has already shown (compare Abstr., 1908, i, 345) that by the action of dibenzylamine on *l*-bromosuccinic acid both a malamic acid and an aspartic acid are produced; the former action proceeds normally, the latter abnormally. It is now shown that a similar partial inversion occurs when methylamine acts on *l*-bromo-succinic acid.

The reacting substances were brought together in a mixture of methyl alcohol and water; the mixture was kept for a week at the ordinary temperature, and was then heated on the water-bath. The products, *d*-β-methylmalamic acid and *l*-methylaspartic acid, were separated by fractional crystallisation of the silver salts. The former acid has $[\alpha]_D$ +13·0°. The latter acid crystallises with $1H_2O$, melts at 183—184°, and forms a salt with one molecule of hydrogen chloride. Its optical behaviour does not correspond with that of aspartic acid. In aqueous solution, methylaspartic acid, in the presence of varying proportions of hydrochloric acid, gave values of $[\alpha]_D$ between −22·6° and −30·8°; in the presence of alkali (5 c.c. of *N*/1-sodium hydroxide added to 0·1105 gram of the anhydrous salt and the solution made up to 20 c.c.), $[\alpha]_D$ −29·8°. As this acid has not so far been brought into simple relationship with the optically active malic acids, its configuration is not regarded as being conclusively established. G. S.

Glutamic Acid and Pyrrolidinecarboxylic Acid. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1910, **64**, 447—459).—As a preliminary to a study of the importance of these substances in metabolism, especially in hæmoglobin formation, a number of salts were prepared and their properties investigated. Monobasic *sodium glutamate*, $C_5H_8O_4NNa$: a crystalline, hygroscopic salt containing 2% water of crystallisation, m. p. 160—170°. Monobasic *calcium glutamate*, $(C_5H_8O_4N)_2Ca$: amorphous. Monobasic *barium glutamate*: hygroscopic, crystallisable from dilute alcohol. Dibasic *copper glutamate*, $C_5H_7O_4NCu,\frac{1}{4}H_2O$: amorphous, greenish-blue. *Potassium glutamate*, $C_5H_8O_4NK$. Monobasic *lead glutamate*, $(C_5H_8O_4N)_2Pb$: hygroscopic.

Attempts were also made to prepare iron salts, but with indifferent results.

Pyrrolidinecarboxylic acid was prepared by heating glutamic acid at 180—190°. It has m. p. 182—184° (corr.), $[\alpha]_D^{20}$ +7·29°. After

treatment with hydrochloric acid gas, a crystalline substance was obtained with the m. p. of glutamic acid hydrochloride. The *calcium* salt, $(C_5H_6O_3N)_2Ca$, was prepared; it is crystalline and hygroscopic. The monobasic *calcium aspartate*, $(C_4H_4O_5N)_2Ca$, and the dibasic *copper aspartate* were also prepared. W. D. H.

Decomposition of Metallic Cyanates by Water. ORME MASSON and IRVINE MASSON (*Zeitsch. physikal. Chem.*, 1910, **70**, 290—314).—The rate of decomposition of the metallic cyanates by water was followed by estimating both the carbonate and unaltered cyanate after heating for definite intervals. The carbonate, if not already precipitated in the course of the reaction, was thrown down by excess of barium nitrate, the precipitate washed, and estimated volumetrically. The cyanate remaining in solution was precipitated by a known excess of silver nitrate, washed, and the unprecipitated silver determined by Volhard's method. All the measurements were made at 80°.

The cyanates of metals forming insoluble carbonates (for example, barium and calcium) are decomposed by water in accordance with the equation: $M(CNO)_2 + 2H_2O = MCO_3 + CO(NH_2)_2$. The change consists of two consecutive reactions: (1) a slow reaction representing the hydrolysis of CNO′ ions, which immediately yield insoluble carbonate and $NH_4^{\cdot}$ ions; (2) the reaction of the $NH_4^{\cdot}$ ions with CNO′ ions to form carbamide. As the second action is relatively rapid, the $NH_4^{\cdot}$ ions are kept at a very small constant concentration. No appreciable effect is produced by the reverse decomposition of carbamide, even if some excess of the latter is added at the outset.

The cyanates of sodium and potassium are decomposed by water according to the equation:

$$4MCNO + 6H_2O = 2M_2CO_3 + (NH_4)_2CO_3 + CO(NH_2)_2,$$

and the ratio of the products thus indicated persists for the whole course of the reaction after a short initial stage. The products of the reaction, more particularly the ammonium carbonate, accelerate the reaction, and if initially added in proportions other than that in which they are produced in the reaction, they alter the relative proportion of the products. Excess of ammonium carbonate tends to increase the carbamide formation relatively to that of ammonium carbonate, whilst excess of metallic carbonate has the converse effect, so that the action is automatically regulated in the direction of the normal ratio. G. S.

Fulminic Acid. LOTHAR WÖHLER (*Ber.*, 1910, **43**, 754—756).—Polemical against the historical accuracy of a monograph by Wieland on fulminic acid (*Ahrensche Sammlung*, Vol. XIV, Nos. 11 and 12). T. S. P.

Dicyanodiamidine Compounds. HERMANN GROSSMANN and B. SCHÜCK (*Ber.*, 1910, **43**, 674—676. Compare Söll and Stutzer, this vol., i, 14).—Commercial dicyanodiamidine sulphate contains no other organic compound as impurity, and may be used for the quantitative estimation of nickel.

Dicyanodiamidinium platinichloride, $(C_2H_6ON_4)_2PtCl_6$, is a yellow, crystalline substance.

Palladiumdicyanodiamidine, $Pd(C_2H_5ON_4)_2,2H_2O$, is obtained as a yellow, crystalline, almost insoluble precipitate on mixing dicyanodiamidine sulphate with palladium chloride and potassium hydroxide. It is soluble in ammonia. E. F. A.

Molybdenum Cyanides. ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1910, **66**, 95—96).—The doubled formula suggested by Rosenheim, Garfunkel, and Kohn (this vol., i, 101) for potassium molybdenum cyanide must be abandoned. Miolati points out that $Mo_2^{V}(CN)_8$ requires just as much oxygen to convert it into molybdic acid as $2Mo^{IV}(CN)_4$, as $Mo_2^{V}(OH)_8$ must first be converted into $Mo_2^{VI}(OH)_{10}$ or $2Mo^{V}(OH)_5$, and then into $2Mo^{VI}(OH)_6$. R. Weinland suggests the formula $K_4Mo^{V}(OH)(CN)_8aq.$, which is possibly correct. C. H. D.

Aliphatic Diazo-salts. KARL A. HOFMANN and RUDOLF ROTH (*Ber.*, 1910, **43**, 682—688. Compare Abstr., 1906, i, 907).—Aminoguanidine dinitrate when diazotised in aqueous solution at 0° with sodium nitrite forms *aminoguanidine diazohydroxide*, $C_2H_7N_{10}\cdot OH$. This is obtained as a colourless, crystalline powder, composed of microscopic, transparent, pointed prisms. It explodes when struck or when heated at 135—140°. It behaves as a diazo-compound; when boiled with water, 3 atoms of nitrogen are eliminated; 15% sulphuric acid liberates 2 atoms. A fourth nitrogen atom is concerned in the formation of aminotetrazolic acid when the diazohydroxide is boiled with water. The diazohydroxide does not form a hydrazine, and yields 4 molecules of ammonia when evaporated with concentrated potassium hydroxide, showing that the amino- and imino-groups of the aminoguanidine molecule remain intact.

The *chloride*, $C_2H_7N_{10}\cdot Cl$, is obtained in colourless, silky, lustrous prisms or needles, and explodes at 140°. When boiled in water, between 3 and 4 atoms of nitrogen are liberated. Water eliminates hydrogen chloride, indicating that the salt is not of the basic type of the aromatic diazonium salts, but belongs to the group of the diazhydroxides, $N:N\cdot OH$. The chloride couples slowly with aromatic amines; α-naphthylamine shows a deep red solution; β-naphthylamine and *m*-phenylenediamine give a brownish-red-yellow coloration. Both hydroxide and chloride when heated with resorcinol and sulphuric acid show an intense violet coloration, which becomes red with a red fluorescence on the addition of excess of ammonia.

The *perchlorate* forms colourless, clear prisms of very explosive nature. It is completely hydrolysed by cold water.

The *nitrate* crystallises in minute, doubly refractive needles; it is less easily exploded.

The *sulphate* is a fine, colourless powder.

The diazohydroxide also combines with bases; with sodium hydroxide it forms an almost colourless solution. After evaporation on the water-bath and the addition of acid, the product can still be coupled. Excess

of silver nitrate causes a precipitate; from the ammoniacal solution the *silver* salt separates in lustrous, centrically-arranged, snow-like crystals, which are very explosive. A *copper* salt is more stable.

E. F. A.

Preparation and Decomposition of the Oximino-derivative of Ethyl Malonylbishydrazoneacetoacetate. CARL BÜLOW and CARL BOZENHARDT (*Ber.*, 1910, 43, 551—563. Compare Abstr., 1908, i, 253; this vol., i, 102).—When ethyl malonylbishydrazoneacetoacetate reacts with nitrous acid, only two of the three reactive methylene groups take part, namely, the two terminal groups, and the product obtained is the dioximino-derivative,

$$CH_2[CO\cdot NH\cdot N:CMe\cdot C(CO_2Et):N\cdot OH]_2.$$

A better yield of the same compound can be obtained by the condensation of V. Meyer's ethyl oximinoacetoacetate (Abstr., 1878, 487) with malonyldihydrazide.

When an excess of nitrous gases is led into a chloroform solution of ethyl malonylbishydrazoneacetoacetate, a molecule of ethyl oximinoacetoacetate is eliminated, and the bisoximino-derivative of malonylhydrazoneacetoacetic acid,

$$OH\cdot N:C(CO_2H)\cdot CMe:N\cdot NH\cdot CO\cdot C(CO_2H):N\cdot OH,$$

is formed according to the equation:

$$CH_2[CO\cdot NH\cdot N:CMe\cdot CH_2\cdot CO_2Et]_2 + 3HNO_2 = EtOH + N_2H_4 + COMe\cdot C(:N\cdot OH)\cdot CO_2Et + OH\cdot N:C(CO_2H)\cdot CMe:N\cdot NH\cdot CO\cdot C(CO_2H):N\cdot OH.$$

Ethyl oximinomalonylbishydrazoneoximinoacetoacetate,

$$CH_2[CO\cdot NH\cdot N:CMe\cdot C(:N\cdot OH)\cdot CO_2Et]_2,$$

crystallises in needles with a nacreous lustre, and has m. p. 200—201°. When boiled for some sixty hours with pure alcohol, it yields malonic acid and the hydrazone of ethyl oximinoacetoacetate, which is immediately transformed into 4-oximino-3-methyl-5-pyrazolone (compare Knorr, Abstr., 1903, i, 660; Betti, Abstr., 1904, i, 533; Wolff, *ibid.*, 722; Bülow and Schaub, Abstr., 1908, i, 687). The same decomposition can be effected by sulphuric acid, sodium hydroxide solution, or ammonium hydroxide, whereas phenylhydrazine reacts with it, yielding hydroxylamine, malonic acid, and 4-*anilinoazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, $C_{16}H_{14}ON_4$, m. p. 154—155°.

Attempts have been made to synthesise ethyl oximinomalonylhydrazoneoximinoacetate from *malonamidehydrazide*,

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

which can be obtained by the action of hydrazine hydrate on an alcoholic solution of ethyl malonamate (Pinner and Oppenheimer, *Ber.*, 1895, 28, 478). The hydrazide crystallises in glistening needles, resembling urea, and has m. p. 126—127°. Ethyl acetoacetate condenses with the hydrazide at 40° in the presence of a few drops of water, yielding *ethyl malonamidehydrazoneacetoacetate*,

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot N:CMe\cdot CH_2\cdot CO_2Et,$$

which crystallises in colourless, felted needles, m. p. 118·5°. It decomposes at 160°, solidifies again at 162°, and then melts at 190—192° to a yellow liquid. It reacts with nitrous acid, yielding

ethyl oximinoacetoacetate according to the equation :

$$NH_2\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot N\colon CMe\cdot CH_2\cdot CO_2Et + 5HNO_2 = COMe\cdot C(\colon NOH)\cdot CO_2Et + 5N + NO + 5H_2O + 2CO_2 + HCN.$$

J. J. S.

Amphoteric Nature of Cacodylic Acid. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1910, **70**, 153—157).—Hantzsch and others regard cacodylic acid as an ordinary weak acid, whilst Johnston (Abstr., 1904, i, 984) has brought forward evidence to show that it is an amphoteric electrolyte. In order to settle the question, the author has determined the $H^{\cdot}$-ion concentration by the diazoacetic ester method in mixtures of the acid with picric acid and nitric acid respectively, and also in aqueous solutions of the acid itself. The results confirm the view of Johnston that cacodylic acid is an amphoteric electrolyte; the value of k_a is about $7\cdot5 \times 10^{-7}$, and that of k_b about $5\cdot6 \times 10^{-13}$ at 25°.

G. S.

New Method of Bromination. Bromination with Aqueous Hypobromous Acid. OTTO STARK (*Ber.*, 1910, **43**, 670—674).—The use of hypobromous acid, prepared by digesting bromine and water with excess of powdered mercuric oxide, in the form of a straw-yellow solution containing about 6·2% of bromine, is suggested as a brominating agent. It suffices to shake this in the cold with benzene, toluene, or benzoic acid to obtain satisfactory yields of monobromobenzene, *o*- and *p*-bromotoluene, and *m*-bromobenzoic acid. Aniline yields tribromoaniline; phenol gives tribromophenol under similar conditions; nitrobenzene resists bromination, as also does phthalic acid.

E. F. A.

Compounds of Aluminium Chloride with Nitro-compounds of Benzene Hydrocarbons and their Derivatives. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 58—94).—The author has investigated the freezing-point diagrams of the systems formed by aluminium chloride with nitrobenzene, and with each of the three chloronitrobenzenes, bromonitrobenzenes, and nitrotoluenes. The m.p.'s of the compounds formed, the two eutectic points, and the compositions corresponding with them are compared with the corresponding data for the systems with aluminium chloride (Abstr., 1909, i, 900).

Nitrobenzene forms the two compounds: (1) $AlCl_3,C_6H_5\cdot NO_2$; and (2) $AlCl_3,2C_6H_5\cdot NO_2$, which crystallises in almost colourless, hygroscopic, rhombic plates, m. p. 25·5° (decomp.).

o-, *m*-, and *p*-Chloronitrobenzenes form compounds of the type $AlCl_3,C_6H_4Cl\cdot NO_2$, having m. p.'s 89°, 104°, and 126° respectively. With the bromonitrobenzenes, compounds of the type

$$AlCl_3,C_6H_4Br\cdot NO_2$$

are formed, the m. p.'s being 100°, 116°, and 145° respectively for the *o*-, *m*-, and *p*-derivatives.

o- and *m*-Nitrotoluenes form compounds of the two types: (1) $AlCl_3,C_6H_4Me\cdot NO_2$, both of which have m. p. 99·5°, and (2) $AlCl_3,2C_6H_4Me\cdot NO_2$, decomposing at 55·1° and 35° respectively. *p*-Nitrotoluene gives only the compound $AlCl_3,C_6H_4Me\cdot NO_2$, m.p. 109°.

Excepting in the case of *m*-bromonitrobenzene, the compounds with aluminium chloride melt at higher temperatures than the corresponding compounds formed by the bromide. The first eutectic points and the compositions at these points differ only slightly for the two series of compounds; in the case of the meta-derivatives, the eutectic mixture always contains a larger proportion of the organic compound than with the corresponding ortho- or para-derivatives.

The temperatures of the second eutectic points are considerably higher for the aluminium chloride than for the bromide systems, although the m. p.'s of the two series of compounds exhibit only small differences. The proportions of organic compound to 1 mol. of aluminium chloride (or bromide) at the second eutectic point vary only slightly, the mean value being 0·653 (or 0·484) mol.

The stability of the aluminium chloride systems is, in general, greater than that of the corresponding aluminium bromide systems, but the solubility curves exhibit similar forms in the two cases.

T. H. P.

The Real State of Metastyrene and the Polymerisation of Styrene by Light and Heat. HANS STOBBE and GEORG POSNJAK (*Annalen*, 1910, **371**, 259—286).—This investigation was undertaken owing to the contradictory nature of the statements of many investigators who have worked on this subject (compare Blyth and Hofmann, *Annalen*, 1845, **53**, 289; Berthelot, *Bull. Soc. chim.*, 1866, [ii], **6**, 294; Krakau, *Ber.*, 1878, **11**, 1260; Lemoine, Abstr., 1898, i, 70; 1900, i, 91; Kronstein, Abstr., 1903, i, 80).

Metastyrene is formed by the action of light or heat on styrene, and is obtained as a white, odourless, amorphous substance by adding alcohol to a solution of the compound in benzene; it does not produce an elevation of the b. p. of a solvent, and is consequently to be regarded as a colloid. The substances described hitherto as metastyrene are mixtures of this substance and styrene; thus, the gelatinous variety is composed of equal parts of these substances, whilst the vitreous modification contains about 20% of styrene.

Metastyrene is quite indifferent towards bromine and potassium permanganate, and is undoubtedly a polymerisation product of styrene, since it passes almost quantitatively into this hydrocarbon at about 320°.

The velocity with which styrene changes into metastyrene under the influence of light and heat has been ascertained by comparison of the viscosity of the substance under observation with that of mixtures of the two substances having a known composition. It is found that (1) the velocity of polymerisation increases with the time; (2) the reaction proceeds in the dark and without the application of heat after it has been started by the action of light, and (3) freshly distilled styrene, under identical conditions, does not polymerise so rapidly as a sample which has been kept in the dark for several days after distillation.

W. H. G.

Liquid and Solid Distyrene. HANS STOBBE and GEORG POSNJAK (*Annalen*, 1910, **371**, 287—302).—Liquid distyrene, which results

from the action of hydrobromic acid or 50% sulphuric acid on cinnamic acid (compare Erlenmeyer, *Annalen*, 1865, **135**, 122; Erdmann, Abstr., 1883, 474), is shown to be $\alpha\gamma$-diphenyl-Δ^{α}-butene, whilst the crystalline distyrene obtained by the destructive distillation of calcium cinnamate (Engler and Leist, Abstr., 1873, 901) and β-truxillic acid (Liebermann, Abstr., 1889, 1194) is $\alpha\delta$-diphenyl-Δ^{α}-butene. Both hydrocarbons yield benzaldehyde when oxidised with chromic acid; the absorption spectra have also been measured, and are represented graphically.

$\alpha\gamma$-Diphenyl-Δ^{α}-butene combines with bromine, forming $\alpha\beta$-dibromo-$\alpha\gamma$-diphenylbutane, m. p. 102° (compare Erdmann, *loc. cit.*), and, when reduced with hydriodic acid and red phosphorus yields, *$\alpha\gamma$ diphenylbutane*, $CH_2Ph\cdot CH_2\cdot CHMePh$, a pale yellow oil, b. p. 295°.

$\alpha\beta$-Dibromo-$\alpha\delta$ diphenylbutane, m. p. 238° (compare Liebermann, *loc. cit.*), when reduced with alcohol and sodium amalgam, yields $\alpha\delta$-diphenylbutane (compare Freund and Immerwahr, Abstr., 1890, 1407).

$\beta\gamma$-Dibromo-$\beta\gamma$-diphenylbutane, $CMePhBr\cdot CMePhBr$, was prepared for the purpose of comparison by treating acetophenonepinacone with acetyl bromide and subsequently with phosphorus pentabromide; it crystallises in small, slender, silky needles, m. p. 140—145° (decomp.).

W. H. G.

Triarylmethyls. II. Triphenylmethyl and Analogues of Triphenylmethyl in the Diphenyl Series. Wilhelm Schlenk, Tobias Weickel, and Anna Herzenstein (*Annalen*, 1910, **372**, 1—20. Compare Abstr., 1909, i, 791).—*Tridiphenylmethyl* (4 : 4′ : 4″-*triphenyltriphenylmethyl*), $C(C_6H_4Ph)_3$, has been prepared by the action of copper bronze (*Naturkupfer* C) on a solution of 4 : 4′ : 4″-triphenyltriphenylmethyl chloride in benzene; it is a dark green, crystalline powder, m. p. 186° (in a sealed tube), solutions of which in organic solvents are deep violet, although thin layers are green. Unlike triphenylmethyl, solutions which have been decolorised by shaking with a small quantity of oxygen do not become coloured when kept; this is due to the fact that, from mol.-wt. determinations, tridiphenylmethyl is present in solution only in the unimolecular, coloured modification. Tridiphenylmethyl combines readily with oxygen, yielding the *peroxide*, $C_{74}H_{54}O_2$, a white, crystalline powder, m. p. 198°.

4-*Phenyltriphenylmethyl* and 4 : 4′-*diphenyltriphenylmethyl* have been prepared by the same method, but do not crystallise readily. The solution of the former in benzene is orange-red; it is decolorised by shaking with a small quantity of oxygen, the *peroxide*, $C_{50}H_{38}O_2$, m. p. 180°, being formed; as in the case of triphenylmethyl, the colour returns when the solution is kept for a short time. The solution of 4 : 4′-diphenyltriphenylmethyl in benzene is red, and likewise contains the coloured and colourless modifications in a state of equilibrium, but in this case the proportion of the latter is very small.

4-Phenyltriphenylmethyl is converted by hydrogen chloride in benzene into 4-phenyltriphenylmethane and 4-phenyltriphenylmethyl chloride, and in this respect differs from triphenylmethyl, which, under similar treatment, has been shown to yield benzhydryltetra-

phenylmethane; it is found, however, that small quantities of triphenylmethane and triphenylmethyl chloride are also formed from triphenylmethyl.

Solutions of 4-phenyltriphenylmethyl chloride, 4 : 4′-diphenyltriphenylmethyl chloride, and 4 : 4′ : 4″-triphenyltriphenylmethyl chloride in liquid sulphur dioxide are orange-red, red, and violet respectively; the unaltered substances are obtained when the sulphur dioxide is allowed to evaporate, except in the last case, when the *additive* product, $(C_6H_4Ph)_3CCl,4SO_2$, is obtained in magenta-like crystals having an intense metallic lustre; a similar *additive* compound is obtained with tridiphenylmethyl. It follows from these observations that the liquid sulphur dioxide does not function merely as a solvent, and, consequently, the assumption that the electrical conductivity of solutions of triphenylmethyl in sulphur dioxide is due to negative and positive triphenylmethyl ions (compare Gomberg, Abstr., 1907, i, 504) is very improbable. It is shown, however, that triphenylmethyl chloride and bromide are dissociated in liquid sulphur dioxide, for it has been found possible to obtain a solution of triphenylmethyl in the cathode chamber by electrolysing these solutions.

The mono-, di-, and tri-phenyl derivatives of triphenylmethyl chloride, in analogy to the alkali halides, turn yellow, orange-red, and violet respectively under the influence of ultraviolet light, probably owing to dissociation into triarylmethyl and halogen; the colour disappears when the substance is subsequently exposed to ordinary light for some time.

The bearing of the observations recorded in the paper on the question of the constitution of triphenylmethyl is discussed; the conclusion is drawn that the constitution of this substance is most suitably represented, not by a quinonoid structural formula, but by the simple formula CPh_3, in which the carbon is tervalent; the unimolecular triarylmethyls are electrically neutral molecules and not ions, for solutions of tridiphenylmethyl in benzene do not conduct.

4-*Phenyltriphenylmethane*, $CHPh_2\cdot C_6H_4Ph$, prepared by reducing the corresponding carbinol with glacial acetic acid and zinc dust, crystallises in long needles, m. p. 112—113°. 4 : 4′-*Diphenyltriphenylmethane*, $CHPh(\cdot C_6H_4Ph)_2$, crystallises with $1C_6H_6$ in leaflets, m. p. 161°. W. H. G.

Triarylmethyls. III. Diphenyldiphenylenecarbinol. WILHELM SCHLENK and ANNA HERZENSTEIN (*Annalen*, 1910, **372**, 21—31. Compare preceding abstract).—In the preceding paper, tridiphenylmethyl is shown to differ from other triarylmethyls in that it exists wholely in solution in the unimolecular state; an attempt to obtain a "triarylmethyl" of an opposite character, namely, one which in solution exists only in the bimolecular state, has been successful.

In the preparation of 4 : 4′ : 4″-triphenyltriphenylcarbinol (compare Abstr., 1909, i, 791), a substance was obtained which examination has shown to be diphenyldiphenylenecarbinol (4-phenylphenyldiphenylenecarbinol); this substance, when treated with acetyl chloride, yields the corresponding chloride, which differs from the analogous triarylmethyl chlorides examined hitherto in that the solutions in

phenol and liquid sulphur dioxide are colourless; further, the solution in benzene when treated with metals remains colourless, the product formed being $\alpha\beta$-bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane. The latter substance differs from hexaphenylethane (triphenylmethyl) and other triarylmethyls, not only in existing in solutions in an undissociated state, but also in not combining readily with oxygen; a peroxide is formed, however, by passing oxygen into the solution during the action of copper on the chloride. The fact that $\alpha\beta$-bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane does not dissociate in solution, shows that the valency acting between the two substituted methyl groups represents a much greater affinity than in the other hexa-arylethanes which have been investigated. In complete agreement with this, diphenyldiphenylenemethyl chloride does not so readily form additive products as other triarylmethyl chlorides (compare Werner, Abstr., 1906, i, 436); thus, tridiphenylmethyl is completely dissociated in benzene, and tridiphenylmethyl chloride forms a moderately stable additive compound with sulphur dioxide (compare preceding abstract); 4-phenyltriphenylmethyl and 4:4′-diphenyltriphenylmethyl are partly dissociated in benzene, whilst additive compounds of the chlorides with sulphur dioxide exist, but are unstable; diphenyldiphenylenemethyl chloride does not form an additive product with sulphur dioxide.

Diphenyldiphenylenemethyl chloride, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!>\!CCl\cdot C_6H_4Ph$, is most readily prepared by the action of 9:9-dichlorofluorene on a solution of diphenyl in carbon disulphide in the presence of aluminium chloride; it crystallises in coarse granules, m. p. 138—140°, and forms intensely coloured, double *salts* with stannic chloride and aluminium chloride; when treated with hot glacial acetic acid and sodium acetate, it yields *diphenyldiphenylenecarbinol*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!>\!C(OH)\cdot C_6H_4Ph$, which crystallises from benzene-light petroleum in stellate groups of slender needles, m. p. 137—139°, and by precipitation from glacial acetic acid in four-sided leaflets, m. p. 149°; the latter compound forms (1) an *additive* compound with fluorenone, crystallising in pale yellow octahedra, m. p. 123°; (2) a *perchlorate*, crystallising in deep blue prisms with a metallic reflex; (3) an *ethyl ether*, m. p. 167°.

$\alpha\beta$-Bisdiphenyl-$\alpha\beta$-bisdiphenylene-ethane,

$$C_6H_4Ph\cdot C(:C_{12}H_8)\cdot C(:C_{12}H_8)\cdot C_6H_4Ph,$$

forms small, colourless prisms, m. p. 175—176°; the *peroxide*, $C_{50}H_{34}O_2$, forms six-sided leaflets, m. p. 193°. W. H. G.

Formation of Colourless Ions from Triphenylmethyl Bromide. ARTHUR HANTZSCH and KURT H. MEYER (*Ber.*, 1910, 43, 336—340).—Triphenylmethyl bromide forms a colourless, electrically conducting solution in pyridine and in acetone; its conducting solution in acetonitrile is yellow at the ordinary temperature, colourless at 0°. Its conductivity in pyridine diminishes rapidly with time, attaining after about one hour a constant value, about half the initial value, and identical with that of *triphenylmethylpyridinium bromide*, $CPh_3\cdot C_5NH_5Br$, a colourless, crystalline substance obtained by the

addition of pyridine to a benzene solution of triphenylmethyl bromide. The change of conductivity is attributed to the conversion of the bromide, which functions initially as a carbonium salt by the addition of pyridine, into an ammonium salt. Triphenylmethyl chloride exhibits a converse behaviour in pyridine, the conductivity slowly increasing with time.

Tri-a-phenyldi-β-methylpropane, $CPh_3{\cdot}CMe_3$, m. p. 185°, is obtained from magnesium *tert.*-butyl chloride and triphenylmethyl bromide in ether by decomposing the initial product with water. C. S.

Structure of Retene. PAUL LUX (*Ber.*, 1910, **43**, 688—692. Compare Abstr., 1908, i, 873).—Retene is either 2-methyl-8-*iso*propyl- or 8-methyl-2-*iso*propyl-phenanthrene [compare following abstract]. The mono-oxime of retenequinone undergoes the Beckmann rearrangement when heated with acetic acid, acetic anhydride, and hydrogen chloride, forming one of the two possible *nitriles* of *methyl*-iso*propyldiphenic acid*, $CN{\cdot}C_6H_3R{\cdot}C_6H_3R'{\cdot}CO_2H$, where R and R′ are the alkyl residues. This acid has m. p. 112—114°, and forms on hydrolysis the corresponding *methyl* iso*propyldiphenamic acid*,

$$NH_2{\cdot}CO{\cdot}C_6H_3R{\cdot}C_6H_3R'{\cdot}CO_2H,$$

m. p. 202—204°.

The nitrile interacts with thionyl chloride, forming the *chloride*, $CN{\cdot}C_6H_3R{\cdot}C_6H_3R'{\cdot}COCl$, m. p. 96—97°, decomp. 150°; it is converted into the *amidenitrile* on treatment with ammonia in benzene solution. This has m. p. 141—142·5°, and is hydrolysed to the *diamide*, $NH_2{\cdot}CO{\cdot}C_6H_3R{\cdot}C_6H_3R'{\cdot}CO{\cdot}NH_2$, or by means of concentrated alcoholic potassium hydroxide to the second *methyl*iso*propyldiphenamic acid*, $CO_2H{\cdot}C_6H_3R{\cdot}C_6H_3R'{\cdot}CO{\cdot}NH_2$, m. p. 194—196°, decomp. 210°. When heated it probably forms the *diphenimide*, $\begin{matrix} R{\cdot}C_6H_3{\cdot}CO \\ | \\ R'{\cdot}C_6H_3{\cdot}CO \end{matrix}\!\!>\!NH$.

E. F. A.

Constitution of Retene and its Derivatives. JOHN E. BUCHER (*J. Amer. Chem. Soc.*, 1910, **32**, 374—382).—In the course of a study of the condensation of acids of the phenylpropiolic series to derivatives of 1-phenyl-2 : 3-naphthalenedicarboxylic acid (Abstr., 1908, i, 791), it was found that the constitution of most of these compounds could be ascertained by converting them into diphenyltetracarboxylic acid or by oxidising them to benzenepolycarboxylic acids. These methods have now been applied to the determination of the constitution of retene (methyl*iso*propylphenanthrene).

When a solution of retenequinone in pyridine is oxidised with potassium permanganate, it is converted into a mixture of acids, containing *3-hydroxy*iso*propyldiphenyl-1 : 1′ : 2′-tricarboxylic acid*,

$$OH{\cdot}CMe_2{\cdot}C_6H_3(CO_2H){\cdot}C_6H_3(CO_2H)_2,$$

which loses water on heating, with formation of a residue soluble in sodium carbonate solution. The formation of this acid from retenequinone shows that two of the carboxyl groups occupy the 1- and 1′-positions, whilst the production of water on heating indicates the presence of another carboxyl group in the 2′-position. As the *iso*propyl residue still remains, the 2′-carboxyl group must have been derived from the methyl group, which therefore occupies the 8-position

in retene. When this tricarboxylic acid is further oxidised, it yields the corresponding tetracarboxylic acid, together with a small quantity of benzene-1 : 2 : 3-tricarboxylic acid. The last mentioned acid is also formed, together with the 1 : 2 : 4-isomeride, by the oxidation of diphenyleneketonedicarboxylic acid which Bamberger and Hooker (Abstr., 1885, 905, 1070) obtained by the oxidation of retene. The production of these two acids shows that retene has one group in the 8-position and the other in either the 2- or 3-position, and excludes the formula proposed by Bamberger and Hooker (*loc. cit.*).

When the mixture of acids obtained by the oxidation of retenequinone is heated with potassium hydroxide at 218° and the resulting acids are reduced with hydriodic acid, a mixture of hydrocarbons is obtained, which, when oxidised with potassium permanganate, yields diphenyl-3-carboxylic acid. The *iso*propyl group in retene must therefore occupy the 2-position, and hence retene is 8-methyl-2-*iso*propylphenanthrene [compare preceding abstract].

It is pointed out that now the constitution of retene has been established, it will be necessary to correct the structural formulæ of its various derivatives. The constitution assigned to abietic acid by Easterfield and Bagley (Trans., 1904, **85**, 1238) is discussed. E. G.

Quantitative Development of the Sandmeyer Reaction. GUSTAV HELLER (*Zeitsch. angew. Chem.*, 1910, **23**, 389—392).—The author has worked out the conditions under which the introduction of chlorine by the Sandmeyer reaction in the case of aniline, and *p*- and *o*-toluidines can be effected almost quantitatively. The most important factor is the concentration of the hydrochloric acid in the solution ; if rather more acid is taken than is recommended by Erdmann (Abstr , 1893, i, 151), the separation of a solid intermediate product does not occur, and the rise in temperature necessary to decompose it may be avoided. The reaction is therefore carried out at a lower temperature than is possible under the conditions given by Erdmann. It is probable that the intermediate compounds formed in these circumstances are very soluble complex salts of cuprous chloride.

R. V. S.

Preparation of 1-Naphthylamine-4 : 7-disulphonic Acid and of -2 : 4 : 7-trisulphonic Acid from 1 : 8-Dinitronaphthalene. FARBWERKE VORM MEISTER, LUCIUS & BRÜNING (D.R.-P. 215338).—When 1 : 8-dinitronaphthalene is reduced in aqueous solution with sodium sulphite, sodium ammonium sulphite, or ammonium sulphite at 70—90°, free alkali is produced ; this results from the entrance of sulphonic groups into the nucleus, and is accompanied by the elimination of a nitro-group.

If the solution is kept neutral, or only slightly alkaline, and the heating continued until the reaction is complete, there separates, when cool, colourless needles of *sodium* or *ammonium* 1-*naphthylsulphamin*-4: 7-*disulphonate*, which on warming with mineral acid yields 1-naphthylamine-4 : 7-disulphonic acid, crystallising from hot water. The more soluble 1-*naphthylsulphamin*-2 : 4 : 7-*trisulphonates* remain in solution, from which, after heating with mineral acid, 1-naphthylamine-2 : 4 : 7-trisulphonic acid can be separated by means of salt. F. M. G. M.

α-*p*-Hydroxyphenylethylamine and the Synthesis of Hordenine, an Alkaloid in Malt Germs. KARL W. ROSENMUND (*Ber.*, 1910, **43**, 306—313).—β-*p*-Methoxyphenylethylamine hydrochloride (this vol., i, 106) is heated with alcoholic potassium hydroxide and methyl iodide at 100°, the product is treated with water and a little ether, the methiodide of the tertiary base is removed, and the mixture of primary, secondary, and tertiary bases, obtained by the evaporation of the filtrate, is heated with acetic anhydride; after the addition of water and ether, the tertiary base alone remains in the aqueous solution as the acetate. It is liberated by sodium hydroxide, extracted with ether, and demethylated by hydriodic acid. The product is β-*p*-hydroxyphenylethyldimethylamine (hordenine),

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$$

(compare Léger, Abstr., 1906, i, 204), its identity with the natural alkaloid being proved, not only by its physical properties, but also by the identity of the methiodides; the latter is also produced by heating β-*p*-methoxyphenylethyltrimethylammonium iodide with hydriodic acid.

α-p-*Methoxyphenylethylamine*, $OMe\cdot C_6H_4\cdot CHMe\cdot NH_2$, b. p. 125—126°/16 mm., is a strongly basic oil obtained by reducing an alcoholic-acetic acid solution of the oxime of *p*-methoxyacetophenone by sodium amalgam; its *hydrochloride* has m. p. 160°. When heated with alcoholic potassium hydroxide and methyl iodide (3 mols.) it yields a *substance*, which melts at 162°, suddenly solidifies again, and then has m. p. 250°. When heated with hydriodic acid, however, α-p-*hydroxyphenylethylamine* is obtained in crystals, m. p. 120—121°. The *hydrochloride* forms needles, m. p. 185°. C. S.

***p*-Tolylethylamine and its Optically Active Forms.** G. A. STENBERG (*Zeitsch. physikal. Chem.*, 1910, **70**, 534—535).—α-p-*Tolylethylamine*, $C_6H_4Me\cdot CHMe\cdot NH_2$, has been prepared by transforming *p*-tolyl methyl ketone into the oxime, and then reducing with sodium amalgam in a solution slightly acidified with acetic acid. It is a colourless liquid, b. p. 204°; $D^{20} = 0·937$.

By repeated fractional crystallisation of its salt with *l*-malic acid (the acid salt), the pure *d*-form of the base was obtained; $D^{20} = 0·9366$; $[\alpha]_D^{20} = +36·57°$. Similarly, the *l*-form has been obtained by fractional crystallisation of the acid salt which the base forms with camphoric acid; $D^{20} = 0·7375$; $[\alpha]_D^{20} = +36·23°$. The sulphates and oxalates of the active salts are considerably more soluble than the racemic salts.

Xylylethylamine is now being investigated; the *l*-form of the salt has already been prepared. G. S.

Isomeric Arylimines of Unsaturated Ketones. FRITZ STRAUS and A. ACKERMANN (*Ber.*, 1910, **43**, 596—608).—Ammonia does not react with the keto-dichloride of *p*-chlorophenyl *p*-chlorostyryl ketone (Abstr., 1909, i, 489), but *p*-nitroaniline reacts in the normal manner, yielding *p*-nitroanilino-*p*-chlorophenyl-*p*-chlorostyrylmethyl chloride, $C_6H_4Cl\cdot CH\!:\!CH\cdot CCl(C_6H_4Cl)\cdot NH\cdot C_6H_4\cdot NO_2$. The chlorine atom of the CCl group is not reactive; for example, the compound dissolves in concentrated sulphuric acid without evolution of hydrogen chloride. It reacts, however, with acids in hydroxylic solvents, yielding the

ketone. The chloride reacts with sodium methoxide or ethoxide, losing hydrogen chloride and yielding the *p*-nitrophenylimine,

$$C_6H_4Cl\cdot CH:CH\cdot C(C_6H_4Cl):N\cdot C_6H_4\cdot NO_2.$$

When *p*-toluidine is used instead of *p*-nitroaniline, an intermediate chloride is not obtained, but the tolylimine is formed immediately. The *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane exists in two isomeric modifications: a yellow and a colourless. They are both stable, and can be crystallised or fused without undergoing transformation; they yield isomeric salts, and can be recovered unaltered from these salts. The two compounds are regarded as stereoisomeric in the same sense as oximes and anils.

p-*Nitroanilino*-p-*chlorophenyl*-p-*chlorostyrylmethyl chloride*,

$$C_{21}H_{15}O_2N_2Cl_3,$$

crystallises in yellow plates, m. p. 118—119°. Its solution in concentrated sulphuric acid is yellowish-red and has a bluish-red dichroism.

The yellow p-*tolylimino*-p-*chlorophenyl*-p-*chlorostyrylmethane*,

$$C_6H_4Cl\cdot CH:CH\cdot C(C_6H_4Cl):N\cdot C_6H_4Me,$$

crystallises in soft, lustrous, yellow needles, m. p. 130—131°, and is the only product formed when the condensation is carried out at the ordinary temperature for some forty hours. The *picrate*,

$$C_{22}H_{17}NCl_2,C_6H_3O_7N_3,$$

crystallises in reddish-yellow needles, m. p. 167—168°, and when boiled with alcohol yields the ketone and *p*-toluidine picrate. The *hydrochloride*, $C_{22}H_{17}NCl_2,HCl$, has m. p. 170—171°. The *isomeric* *p*-tolylimine is formed when the reacting substances are left together for some weeks; it crystallises in colourless, glistening plates, m. p. 144—145°, and is not so readily soluble in most solvents or so readily burnt as is the yellow isomeride. The *picrate*,

$$C_{22}H_{17}NCl_2,OH\cdot C_6H_2(NO_2)_3,$$

forms heavy, yellow crystals, m. p. 102—103° (decomp.). These crystals contain benzene of crystallisation, and, after heating until constant in weight, have m. p. 116—117°. It is not decomposed when boiled with alcohol. The *hydrochloride* forms snow-white needles, m. p. 100—101°, and when heated at 110—115° decomposes, yielding *p*-chloroacetophenone and *p*-chlorophenyl *p*-chlorostyryl ketone.

J. J. S.

Coloured Additive Products of Aromatic Amines. The Question of the Mechanism of Substitution in the Benzene Nucleus. VII. Heinrich Wieland and Ernst Wecker (*Ber.*, 1910, **43**, 699—712. Compare Abstr., 1907, i, 1076, and following abstract).—The authors have more fully investigated the strongly coloured, unstable compounds of tertiary and secondary amines with bromine and with the chlorides of the metalloids. They consider that these compounds are quinonoid additive products of the type $NAr_2Br:C_6H_4:MeBr$, which undergo spontaneous rearrangement, forming compounds with substituted benzene nuclei. The reaction in the case of the blue bromide of tri-*p*-tolylamine is expressed by the equation:

$$2N(C_6H_4Me)_3Br_3 = N(C_6H_3BrMe)_3 + N(C_6H_4Me)_3 + 3HBr.$$

Tri-*p*-tolylamine when treated with bromine in benzene solution at

$-15°$ yields a *tribromide*, $N(C_7H_7)_3Br_3$, which forms dark blue, crystalline scales. When a chloroform solution of the substance is kept at the ordinary temperature, *tribromotri*-p-*tolylamine*, m. p. 190°, and tri-*p*-tolylamine are formed. The dibromotri-*p*-tolylamine, m. p. 160—165°, formerly described (*loc. cit.*) is a mixture of tribromotri-*p*-tolylamine and tri-*p*-tolylamine. *Tri* p-*anisylamine*, prepared by Goldberg's method (Abstr., 1908, i, 17), has m. p. 94·5°. With bromine it yields a *tribromide*, $N(C_6H_4{\cdot}OMe)_3Br_3$, which crystallises in dark violet laminæ, and is very stable. In chloroform solution it slowly decomposes, forming *tribromotri*-p-*anisylamine*, m. p. 179°, and tri-*p*-anisylamine. Tri-*p* anisylamine also forms a deep blue, crystalline *compound* with antimony pentachloride. *Diphenyl*-p-*anisidine*, $NPh_2{\cdot}C_6H_4{\cdot}OMe$, prepared by Goldberg's method, has m. p. 104°. The compounds of this substance with bromine and antimony pentachloride could not be isolated.

Diphenylamine and di-*p*-tolylamine do not give coloured additive products with bromine or antimony pentachloride; phenyl-*p*-anisidine gives colorations indicating the formation of such compounds, and from the solution, *tribromophenyl*-p-*anisidine*, m. p. 100·5°, is obtained. Phenyl-*p*-anisidine (compare Willstätter and Kubli, Abstr., 1909, i, 976) was prepared from aceto-*p*-anisidide by Goldberg's method. In the case of di-*p*-anisylamine, the colorations observed are abnormal, owing to the formation of some anisazonium bromide, which is red. The additive *bromide* can be obtained by working in ethereal solution as a dark bluish-green, flocculent precipitate, which can be filtered. On dissolving it in chloroform, rearrangement occurs so rapidly that the solution is colourless unless strongly cooled. In solvents other than ether, di-*p*-anisylamine and bromine directly yield *dibromodi*-p-*anisylamine*, m. p. 79°. When this is treated with a further quantity of bromine in benzene-chloroform solution, a green, crystalline, stable *dibromide*, $C_{14}H_{13}O_2NBr_2,Br_2$, is formed, m. p. 104° (decomp.). In chloroform solution it undergoes rearrangement, yielding, besides dibromodi-*p*-anisylamine, a mixture of *tribromodi*-p-*anisylamine*, m. p. 135·5°, and *tetrabromodi*-p-*anisylamine*, m. p. 183°. A *compound* of di-*p*-anisylamine and antimony pentachloride, $C_{14}H_{15}O_2N,SbCl_5$, is formed on mixing chloroform solutions of the two substances. It crystallises in dark steel-blue prisms, m. p. 116—118°, and is stable. From it, anisazonium chloride and di-*p*-anisyldihydroanisazine can be prepared (compare Abstr., 1908, i, 1015). R. V. S.

Oxidation of *p*-Anisidine and of Dimethyl-*p*-anisidine. HEINRICH WIELAND [with ERNST WECKER] (*Ber.*, 1910, **43**, 712—728. Compare preceding abstract.)—The fact that the methoxylated amines yield coloured additive products with bromine, whilst the amines themselves do not, leads to the supposition that these additive products may be oximonium compounds of the type

$$OMe{\cdot}C_6H_4{\cdot}NHBr{:}C_6H_4{:}OBrMe.$$

The action of bromine on *p*-anisidine and on dimethyl-*p*-anisidine at low temperatures effects the removal of the methoxyl group with remarkable ease, the ultimate product of the oxidation being quinone.

The formation of *meri*-quinonoid and quinonoid bromine compounds as intermediate products also occurs, although these are less stable than the corresponding nitrogen derivatives (compare Willstätter and Piccard, Abstr., 1908, i, 475, 915).

p-Anisidine is oxidised by ferric chloride, chromic acid, hypochlorous acid, bromine, and other oxidising agents in acid solution with formation of a violet dye, which yields a leuco-base on reduction, indicating that several molecules of the amine have become united (compare Willstätter and Piccard, Abstr., 1909, i, 517). In acetic acid solution in the presence of sodium acetate, bromine water oxidises all the anisidine to the violet dye, which soon decomposes. When the oxidation is effected by bromine water at a low temperature, however, a pure blue coloration develops, which gradually becomes violet. It is probable that the blue colour is due to the *meri*-quinonoid additive product $\{OBrMe\colon C_6H_4\colon NH_2Br,OMe\cdot C_6H_4\cdot NH_2\}$. The violet dye only appears in acid solution when insufficient bromine is present; when the oxidation by bromine water in faintly acid solution is rapid and complete, the *p*-anisidine is converted almost quantitatively (98%) into quinone. In this reaction 2 molecules of free acid are formed, showing that hydrolysis of the methoxyl group occurs; this confirms the theory as to the primary formation of a quinonoid oximonium salt.

Aminophenol also yields quinone quantitatively when oxidised with bromine water under the above conditions (compare Willstätter and Dorogi, Abstr., 1909, i, 535), and in this case, also, the intermediate formation of quinonemonoimine (Willstätter and Pfannenstiel, Abstr., 1905, i, 69) is probable.

When treated with bromine in chloroform solution, *p*-anisidine yields a *dibromo*-p-*anisidine*, which crystallises in long needles, m. p. 81°. The bromination is accompanied by the development of an evanescent, blue colour, and when it is effected in ethereal solution, an unstable blue *compound* (perhaps the primary quinonoid product) can be isolated.

Dimethyl-*p*-anisidine (compare Griess, Abstr., 1880, 636) is obtained by methylating *p*-anisidine with methyl sulphate. It has m. p. 49° (Griess: 48°). The *chloride, bromide,* and *picrate* crystallise well. When the base is treated gradually with bromine in chloroform solution, a vivid red coloration is first produced, which gradually changes to a blue colour; eventually, the quinonoid *perbromide*, $OBrMe\colon C_6H_4\colon NMe_2Br_2$, is precipitated. It crystallises in small, lustrous, green laminæ, m. p. 49—50°, and on reduction yields dimethyl-*p*-anisidine. Its aqueous solution (which is orange) rapidly decomposes into quinone, dimethylamine hydrobromide, hydrobromic acid, and methyl alcohol. Oxidation of dimethyl-*p*-anisidine in aqueous solution with one molecule of bromine (in the form of bromine water) yields a quinonoid bromide of dimethylaminophenol, $NMe_2Br\colon C_6H_4\colon O$, in solution, for, on reducing the liquid, dimethylaminophenol is obtained. If a second molecule of bromine is added, however, the fairly stable, yellow *perbromide*, $NMe_2Br\colon C_6H_4\colon OBr_2$, m. p. 90°, is precipitated. On reduction, this yields almost quantitatively dimethyl-*p*-aminophenol, m. p. 78° (von Pechmann, Abstr., 1900, i, 173, gave

74—76°). When left in contact with water, the perbromide decomposes into quinone, dimethylamine hydrobromide, and bromine.

The estimation of quinone is effected by reducing to quinol, and titrating the latter with iodine in the presence of sodium hydrogen carbonate. On acidifying, the quinone liberates the iodine again, and, as a control, this may be titrated with thiosulphate. This is of value when traces of other oxidisable substances are present. The quinone in ethereal solutions may also be estimated by a modification of Nietzki's method.

Bromine is best recognised in the presence of quinonoid compounds and mineral acid by adding sodium acetate solution before testing with potassium iodide and starch paper, which is then only affected by the free halogen. R. V. S.

Carbodiphenylimide. KARL SCHALL (*J. pr. Chem.*, 1910, [ii], **81**, 191—192).—The author disputes some of the statements concerning γ-carbodiphenylimide made in a footnote in Busch, Blume, and Punge's paper on carbodiphenylimide (Abstr., 1909, i, 565). C. S.

Δ-$^{1:5}$-Dihydrophenol. [Δ^2-*cyclo*-Hexenone.] LEO TSCHUGAEFF (*J. pr. Chem.*, 1910, [ii], **81**, 188—189).—Polemical. A reply to Kötz and Grethe (this vol., i, 24). The author claims priority for the method used to convert *cyclo*-hexanon-2-ol into $\Delta^{1:5}$-dihydrophenol, and dissents from these authors representing the xanthogenate as containing ⁚C(OH)·CS·SMe in preference to the constitution, ⁚CH·O·CS·SMe, usually accepted. C. S.

Phenol and *m*-Nitrophenol as Acids. HARALD LUNDÉN (*Zeitsch. physikal. Chem.*, 1910, **70**, 249—255).—The acid dissociation constant, k_a, of phenol has been determined by measuring the electrical conductivity of solutions of the ammonium salt; the values are $k_a \times 10^{10} =$ 0·56 at 10°, 0·66 at 15°, 0·97 at 25°, 1·51 at 40°, and 2·05 at 50°. These values have been confirmed by direct determinations of the conductivity of aqueous solutions of phenol, and are also in good agreement with the results obtained by Buch (Abstr., 1908, i, 259).

The dissociation constant of *m*-nitrophenol has also been determined by conductivity measurements with carefully purified aqueous solutions; the values are $k_a \times 10^9 = 3·31$ at 10°, 3·91 at 15°, 5·33 at 25°, 7·72 at 40°, and 9·54 at 50°.

From the data for phenol, the heat of neutralisation with ammonia and the heat of dissociation have been calculated in the usual way; the value of the former is $7605 - 6·5t$ cal., and of the latter, $-7095 + 43·5t$ cal. per mol. Both values are in excellent agreement with the direct determinations of Berthelot (1873).

The heat of neutralisation of *m*-nitrophenol is $8520 - 2·1t$ cal.; the heat of dissociation, $-6180 + 47·9t$ cal.

The data for the influence of temperature on the total and free energy of the above changes are tabulated. G. S.

New Method of Formation of Ethers of Glycerol and Phenols. PETAR ŽIVKOVIĆ (*Monatsh.*, 1908, **29**, 951—958).—A mixture

of a phenol or naphthol (1 part), glycerol (2 parts), and anhydrous sodium acetate (1 part), contained in a flask, in an atmosphere of coal gas, is heated for twelve to twenty hours by the vapour of ethyl benzoate. In the case of the phenols, the benzene extract of the product is directly precipitated with light petroleum; when dealing with α-naphthol, the mass is boiled with water and dried before being treated with benzene. In addition to glycerol phenyl ether, the following mono-ethers have been obtained: the *o-tolyl ether*, $C_7H_7 \cdot O \cdot C_3H_5(OH)_2$, m. p. 66°; the *m-tolyl ether*, m. p. 65°; the *p-tolyl ether*, m. p. 73—74°; the *α-naphthyl ether*, m. p. 91—92°; *β-naphthyl ether*, m. p. 109—110°. None of the ethers give a colour reaction with ferric chloride, but form brown or green solutions in concentrated sulphuric acid when treated with potassium nitrite, which become green or red by dilution and the addition of alkali. C. S.

Amino-alcohols. Derivatives of Glycerol and Phenyl Ethers. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1910, [vii], 1, 55—61, 97—103).—The complex ethers obtained by the condensation of epichlorohydrin with phenols have been studied, and especially their reaction with amines.

When phenol or sodium phenoxide is heated in a closed tube with epichlorohydrin, the three chief products formed are: (1) phenyl glycide ether, $OPh \cdot CH_2 \cdot CH {<}{\overset{CH_2}{\underset{O}{|}}}$, b. p. 242·5°/755 mm. (compare Rössing, Abstr., 1886, 345; Lindemann, Abstr., 1891, i, 1198; Cohn and Plohn, Abstr., 1907, i, 605); (2) γ-chloro-β-hydroxy-α-phenoxypropane, $OPh \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$, b. p. 170°/21 mm. (compare Lindemann, *loc. cit.*; Fischer and Krämer, Abstr., 1908, i, 858), and (3) glycerol diphenyl ether (Lindemann, *loc. cit.*). In some cases a small amount of *diphenoxydipropanol oxide*, $[OPh \cdot CH_2 \cdot CH(OH) \cdot CH_2]_2O$, m. p. 81°, b. p. 300—305°/16 mm., is formed; it crystallises in colourless spangles.

Phenyl glycide ether reacts with water to form glycerol phenyl ether, m. p. 69°, and with alcohol to form *glycerol phenyl ethyl ether*, $OPh \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OEt$, b. p. 158—160°/25 mm., a colourless, inodorous liquid. With magnesium ethyl bromide, *phenoxypropylene bromohydrin*, b. p. 160—162°/18 mm., is formed (compare Abstr., 1907, i, 817), but with magnesium phenyl bromide, *β-hydroxy-γ-phenoxy-α-phenylpropane*, $OPh \cdot CH_2 \cdot CH(OH) \cdot CH_2Ph$, m. p. 91—92°, crystallising in spangles, is obtained.

In the action of epichlorohydrin on (*a*) *p*-cresol and (*b*) α-naphthol, the corresponding glycide ethers described by Lindemann (*loc. cit.*) are produced, and, in addition, *glycerol di*-p-*tolyl ether* in the one case and *glycerol di-α-naphthyl ether* (m. p. 116°) in the other.

The product obtained by the action of catechol on epichlorohydrin is not diglycidylcatechol as Lindemann supposed (*loc. cit.*), but is identical with Moureu's substance obtained by condensing sodium catechol with αβ-dibromohydrin.

The *glycide ether*, prepared in an analogous manner from guaiacol, has b. p. 170°/16 mm. and m. p. 79·5°, whilst that from thymol boils at 180°/20 mm., melts at 88°, and crystallises in colourless needles.

By the action of sodium *p*-nitrophenoxide on dichlorohydrin, *glycerol di*-p-*nitrophenyl ether*, $OH\cdot CH(CH_2\cdot O\cdot C_6H_4\cdot NO_2)_2$, m. p. 122—123°, crystallising in bright yellow needles, is obtained, together with p-*nitrophenyl glycide ether*, m. p. 69°, which forms yellow tablets.

Phenyl glycide ether reacts with ammonia to form *diphenoxypropanolamine*, $NH[CH_2\cdot CH(OH)\cdot CH_2\cdot OPh]_2$, m. p. 97—98°; its *hydrochloride* has m. p. 175°.

The following amino-alcohols have been obtained in like manner by the action of appropriate amines on the glycide ethers described above.

γ-*Dimethylamino-α-phenoxypropanol*, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2$, has b. p. 161°/13 mm. or 169°/25 mm.; the *picrate*, m. p. 105°, crystallises in spangles; the *hydrochloride* of the *benzoyl* derivative, m. p. 166°, the *ethyl bromide* derivative, m. p. 112°, and other similar compounds were prepared. The corresponding γ-*anilino*-derivative,

$$OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHPh,$$

has m. p. 57°, and the analogous γ-*phenetidino*-compound, m. p. 95°, both crystallise in colourless needles.

γ-*Dimethylamino-α*-p-*tolyloxypropanol*, b. p. 175—176°/10 mm., yields a *benzoyl* derivative, the *hydrochloride* of which has m. p. 156° and crystallises in slender needles.

γ-*Dimethylamino-α-guaiacylpropanol*, m. p. 61°, yields a *methiodide*, m. p. 114°, and a *benzoyl* derivative, the *hydrochloride* of which has m. p. 142°.

γ-*Dimethylaminonaphthoxypropanol*, m. p. 81—82°, b. p. 217°/11 mm., crystallises in slender needles, and yields a *methiodide*, m. p. 204°.

γ-*Dimethylamino-α*-p-*nitrophenoxypropanol* exists in two forms (tablets and prisms), both having m. p. 81—82°; the *picrate*, m. p. 153°, and the *hydrochloride* of the *benzoyl* derivative, m. p. 181°, were prepared.

γ-*Dimethylamino-α-thymoxypropanol*, b. p. 177°/11 mm., crystallises on cooling, and gives a *methiodide*, m. p. 160°.

The methods of preparing these substances are described in some detail in the original. As a rule, these amino-alcohols exhibit antipyretic and analgesic properties, but, owing to their cardiac action, they are unsuitable for therapeutic use in this way. T. A. H.

Preparation of Tribromocatechol. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 215337).—When catechol is treated with 3 mols. of bromine in acetic acid solution, no tribromocatechol is formed, the product consisting of a mixture of the di- and tetra-bromo-derivatives.

Tribromocatechol, m. p. 138—139°, is obtained by the action of bromine in chloroform on a suspension of catechol in the same solvent; it is colourless, odourless, and insoluble in water, but readily soluble in alcohol, ether, or acetone, and contains 1 mol. of water of crystallisation. It is employed therapeutically, and also in the preparation of dyes.

F. M. G. M.

Action of Phosphorus Trichloride on Guaiacol. PIERRE DUPUIS (*Compt. rend.*, 1910, **150**, 622—623).—Three compounds may be formed when guaiacol is heated with phosphorus trichloride

according to the proportions in which these substances react. *Guaiacylphosphorus chloride*, $OMe\cdot C_6H_4\cdot O\cdot PCl_2$, prepared at 115—120°, is a colourless, refractive liquid, b. p. 135°/13 mm., n_D^{21} 1·568. When dissolved in dry ether and treated with chlorine, a yellow *tetrachloride*, $OMe\cdot C_6H_4\cdot O\cdot PCl_4$, is formed, which is converted by sulphur dioxide into Auger's compound, $OMe\cdot C_6H_4\cdot O\cdot POCl_2$ (Abstr., 1908, i, 529).

Diguaiacylphosphorus chloride, $P(O\cdot C_6H_4\cdot OMe)_2Cl$, has b. p. 235°/13 mm., n_D^{21} 1·586 and forms a *trichloride*, $P(O\cdot C_6H_4\cdot OMe)_2Cl_3$, from which diguaiacyl phosphoryl chloride may be obtained by the action of sulphur dioxide. Triguaiacyl phosphite, $P(O\cdot C_6H_4\cdot OMe)_3$, b. p. 275—280°/13 mm., solidifies on cooling, forming octahedra, m. p. 59°. This is not identical with Ballard's compound obtained by the action of phosphorus trichloride on the sodium derivative of guaiacol (D.R.-P. 95578).

The foregoing compounds are soluble in ether and benzene, and undergo decomposition when treated with water. W. O. W.

Some Derivatives of Phloroglucinol and a New Synthesis of Benzoresorcinol [2 : 4 - Dihydroxybenzophenone]. EMIL FISCHER (*Annalen*, 1910, **371**, 303—318).—2 : 4-Dihydroxybenzophenone may be prepared by hydrolysing the product formed by the interaction of benzene, aluminium chloride, and 2 : 4-dimethylcarbonatobenzoyl chloride (compare Abstr., 1909, i, 161).

Phloroglucinolcarboxylic acid reacts with only 1 mol. of methyl chlorocarbonate in *N*-sodium hydroxide solution; all attempts to obtain the corresponding trimethylcarbonato - derivative were unsuccessful; consequently 2 : 4 : 6-trihydroxybenzophenone could not be prepared in the same way as 3 : 4 : 5-trihydroxybenzophenone (compare Abstr., 1909, i, 309). Attempts to prepare 2 : 4 : 6-trihydroxybenzophenone by other methods were unsuccessful, but many new benzoyl derivatives of phloroglucinol have been obtained, the most interesting of which are the dibenzoyl derivatives of phloroglucinol dialkyl ethers; these probably have the constitution represented by one of the the following formulæ: $\begin{matrix} CBz{:}C(OR)\cdot CH \\ | \qquad\qquad || \\ C(OH){:}CBz\cdot C\cdot OR \end{matrix}$ or $\begin{matrix} CBz{:}C(OR)\cdot CBz \\ | \qquad\qquad || \\ C(OH){:}CH\cdot C\cdot OR' \end{matrix}$, and, similarly to hydrocotoin (*C*-benzoylphloroglucinol dimethyl ether), are stable towards warm aqueous alkali; in this respect they differ from triacetyl*cyclo*hexanetrione and its tribenzoyl derivative (compare Heller, Abstr., 1909, i, 656).

1 : 3 : 5-*Trimethylcarbonatobenzene*, $C_6H_3(O\cdot CO_2Me)_3$, prepared by acting on a solution of phloroglucinol in a *N*-solution of sodium hydroxide with methyl chlorocarbonate, crystallises in long, glistening prisms, m. p. 99—100° (corr.); 4-*methylcarbonato*-2 : 6-*dihydroxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$, similarly prepared from phloroglucinolcarboxylic acid, crystallises in tufts of flexible needles, m. p. 162° (corr., decomp.).

Benzoylphloroglucinolcarboxylic acid, $OBz\cdot C\Big<\begin{matrix} CH\cdot C(OH) \\ CH{:}C(OH) \end{matrix}\Big>C\cdot CO_2H$, prepared from phloroglucinolcarboxylic acid and benzoyl chloride, crystallises in small prisms, m. p. 195° (corr., decomp.); the *silver* salt is a colourless, crystalline powder; the acid loses carbon dioxide when

heated at 200°, yielding *benzoylphloroglucinol*, $C_{13}H_{10}O_4$, which forms slender leaflets and needles, m. p. 198—199° (corr.).

O-*Benzoylphloroglucinol diethyl ether*, $C_6H_3(OEt)_2{\cdot}OBz$, is formed by acting on phloroglucinol diethyl ether with benzoyl chloride and alkali; it crystallises in colourless, slender, pointed prisms and needles, m. p. 84° (corr.), and when heated with benzoyl chloride and zinc chloride in benzene yields *tribenzoylphloroglucinol diethyl ether*, $CHBz_2(OEt_2){\cdot}OBz$, which crystallises in microscopic, long, slender plates, m. p. 163—164° (corr.); the latter substance is converted by an alcoholic solution of potassium hydroxide under pressure at 100° into C-*dibenzoylphloroglucinol diethyl ether*, $C_6HBz_2(OEt)_2{\cdot}OH$, which forms slightly yellow, microscopic, rhomboidal leaflets, m. p. 156° (corr.); the *potassium* salt forms glistening, pale yellow leaflets; the *sodium* salt crystallises in slender needles.

Tribenzoylphloroglucinol dimethyl ether, $C_{29}H_{22}O_6$, may be prepared by treating either the monobenzoyl compound or hydrocotoin with benzoyl chloride and zinc chloride in benzene; it crystallises in microscopic plates, m. p. 198° (corr.); C-*dibenzoylphloroglucinol dimethyl ether*, $C_{22}H_{18}O_5$, crystallises in microscopic needles and plates, m. p. 170° (corr.); the *potassium* salt, $C_{22}H_{17}O_5K$, forms yellow, microscopic plates.

W. H. G.

Derivatives of Triphenylcarbinol. II. ADOLF VON BAEYER [and, in part, AICKELIN, CARL DIEHL, HALLENSLEBEN, and HERMANN HESS] (*Annalen*, 1910, **372**, 80—151. Compare Abstr., 1907, i, 757).—The present communication contains the results of a systematic investigation of the binary derivatives of triphenylcarbinol, namely, those containing two hydroxyl or amino-groups in at least one of the benzene nuclei.

I. *Binary Dihydroxy-derivatives.*—(1) *Dihydroxytriphenylcarbinols.*—2 : 5-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3$, prepared by Grignard's reaction from ethyl 2 : 5-dihydroxybenzoate and bromobenzene, has m. p. 136°; it crystallises with $\frac{1}{2}C_6H_6$ in colourless, glistening leaflets, m. p. 110° (decomp.); a green *substance*, which probably has the formula $C_6H_3(OH)_2{\cdot}CPh_2Cl,HCl$, is obtained by passing hydrogen chloride into an ethereal solution of the carbinol and evaporating in a vacuum desiccator over potassium hydroxide; it dissolves in ether, forming a colourless solution of the carbinyl *chloride*, $C_6H_3(OH)_2{\cdot}CPh_2Cl$, which, when treated with alkalis, assumes a transient, blue colour, owing to the formation of an unstable *o*-fuchsone with a hydroxyl group in the quinonoid ring, $\begin{array}{l}C(ONa){:}CH{\cdot}C{:}CPh_2\\ |\qquad\qquad\quad\ |\\ CH{=\!=}CH{\cdot}C{:}O\end{array}$.

The compounds described immediately were prepared in an unsuccessful attempt to obtain a *p*-fuchsone with a hydroxyl group in the quinonoid nucleus.

Methyl 2 : 4-*dihydroxybenzoate*, $C_8H_8O_4$, crystallises in colourless, glistening rhombohedra, m. p. 117—118°; when treated with magnesium phenyl bromide, it yields a red tar, from which 2 : 4-dihydroxytriphenylcarbinol could not be isolated.

2 : 4-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3$, is prepared by Grignard's reaction from 2 : 4-dihydroxybenzophenone and bromobenzene; it

crystallises in colourless prisms, m. p. 124° (decomp.), and is hydrolysed by aqueous sodium hydroxide, yielding benzophenone, resorcinol, 2 : 4-dihydroxybenzophenone, and benzene; the *perchlorate*, $C_{19}H_{15}O_6Cl$, forms large, brown plates, and explodes slightly when heated; all attempts to isolate the corresponding fuchsone were unsuccessful; when a solution of the carbinol in nitrobenzene is heated at 100°, it yields a *substance*, which crystallises in dark brown needles, m. p. 264°.

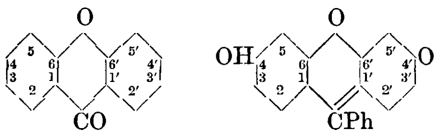
2 : 4-*Dihydroxy*-4′-*methoxytriphenylcarbinol*, $C_{20}H_{18}O_4$, prepared from 2 : 4-dihydroxy-4′-methoxybenzophenone and bromobenzene, crystallises in colourless prisms, m. p. 138—139° (decomp.).

(2) *Dihydroxydiphenylphthalides.*—2 : 4-Dihydroxydiphenylphthalide is best prepared by the action of concentrated sulphuric acid on a cold fused mixture of *o*-benzoylbenzoic acid and resorcinol; contrary to von Pechmann (Abstr., 1882, 184), it has m. p. 198—199°, and does not give a coloration when the solution in glacial acetic acid is treated with concentrated hydrochloric acid; the solution in aqueous alkalis is orange, and probably contains the fuchsone derivative,

$$CO_2Na\cdot C_6H_4\cdot CPh{:}C{<}\begin{matrix}CH{=\!=}CH\\ C(OH){:}CH\end{matrix}{>}CO.$$

3 : 4-*Dihydroxydiphenylphthalide*, $C_{20}H_{14}O_4$, forms colourless prisms, m. p. 160—161°. 2 : 5-*Dihydroxydiphenylphthalide* crystallises in needles and prisms, m. p. 246—247° (decomp.), and dissolves in aqueous sodium hydroxide in the absence of oxygen, forming a blue solution which becomes colourless when kept, but in the presence of air turns brown, owing to oxidation; the blue solution undoubtedly contains the *salt*, $CO_2Na\cdot C_6H_4\cdot CPh{:}C{<}\begin{matrix}CO{-\!-}CH\\ CH{:}C(OH)\end{matrix}{>}CH$; the corresponding *quinone*, $C_{20}H_{12}O_4$, obtained by treating an ethereal solution of the dihydroxy-compound with silver oxide, forms aggregates of dark yellow crystals, m. p. 147°; the latter substance forms a *quinhydrone* with quinol; the dihydroxy-compound also forms a *quinhydrone* with *p*-benzoquinone, but not with its own quinone.

II. *Unitary-binary Trihydroxy-derivatives.* — *Trihydroxytriphenylcarbinols.* — Since xanthen is a saturated compound, the author proposes to designate this substance xanthan; the use of the annexed system of numbering the positions in xanthone and resorcinolbenzein is advocated [but is not adopted in this abstract] as the author dissents from that used in Beilstein [and in this Journal].



o-3-*Methoxyphenoxybenzoic acid*, $OMe\cdot C_6H_4\cdot O\cdot C_6H_4\cdot CO_2H$, prepared by Ullmann's method (Abstr., 1905, i, 597) from *o*-chlorobenzoic acid and 3-methoxyphenol, crystallises in colourless, silky needles, m. p. 132°; when treated in benzene with phosphorus pentachloride and subsequently with aluminium chloride, it yields 3-*methoxyxanthone*,

$$C_6H_4{<}\begin{matrix}O{-}C{:}CH\cdot C\cdot OMe\\ CO\cdot C{:}CH\cdot CH\end{matrix}$$

which forms tufts of colourless needles or leaflets, m. p. 132°. The latter substance is converted by magnesium phenyl bromide into

3-methoxy-9-phenylxanthen-9-ol, $C_6H_4{<}\begin{smallmatrix}\text{——O——}\\ CPh(OH)\end{smallmatrix}{>}C_6H_3\cdot OMe$, which crystallises in colourless prisms, m. p. 127°, and, when treated with a solution of aluminium chloride in antimony trichloride, yields phenylfluorone, m. p. 207° (compare Kehrmann and Dengler, Abstr., 1908, i, 1002).

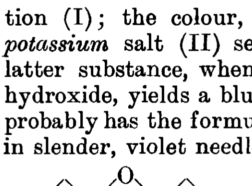
2-Methoxyxanthone has m. p. 135° (compare Ullmann, *loc. cit.*); *2-methoxy-9-phenylxanthen-9-ol*, $C_{20}H_{16}O_3$, crystallises in short prisms and plates, m. p. 136°; 2-hydroxy-9-phenylxanthen-9-ol has m. p. 170° (compare Kropp and Decker, Abstr., 1909, i, 248).

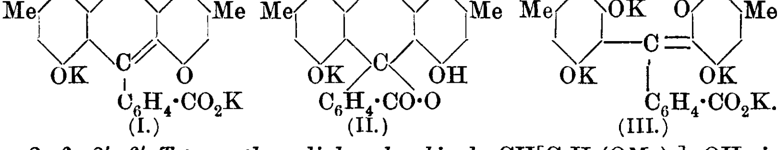
4-Methoxy-9-phenylxanthen-9-ol crystallises in colourless prisms, m. p. 172°; *4-hydroxy-9-phenylxanthen-9-ol*, $C_{19}H_{14}O_3$, forms bundles of small needles, m. p. 162°.

III. *Binary Tetrahydroxy-derivatives.*—(1) *Resorcinol group in the* o:p-*position.*—Fluorescein hydrochloride (compare Gattermann, Abstr., 1899, i, 513) is readily obtained in hexagonal leaflets by treating fluorescein with concentrated hydrochloric acid.

The nature of the changes which take place when fluorescein is treated with alkali is discussed. The conclusion is drawn that the blue salts of the fluorescein group result from the hydrolytic fission of the oxygen-bridge of the xanthone nucleus, and contain, at least in the rhodamine series, an ortho-quinonoid group. Since fluorescein is a carboxylic acid of resorcinolbenzein, it seemed probable that the latter substance would yield a violet salt when warmed with aqueous potassium hydroxide; under certain conditions an evanescent, violet coloration is obtained, which seems to point to the formation of an unstable violet salt with fission of the oxygen-bridge.

(2) *Resorcinal group in the* o : o′-*position.*—Meyer's α-orcinolphthalein (Abstr., 1897, i, 70) undoubtedly has the annexed constitution, since it corresponds completely with *vic.*-resorcinolbenzein (1 : 8-dihydroxy-9-phenylxanthen-9-ol) in properties; it is proposed, therefore, to designate this compound *vic.*-orcinolphthalein. The addition of alcoholic potassium hydroxide to an alcoholic solution of *vic.*-orcinolphthalein produces a violet coloration, probably owing to the formation of a *salt* having the constitution (I); the colour, however, disappears rapidly, and a colourless *potassium* salt (II) separates in elongated, rectangular prisms; the latter substance, when warmed with concentrated aqueous potassium hydroxide, yields a blue *potassium* salt, crystallising in prisms, which probably has the formula (III); an analogous *sodium* salt, crystallising in slender, violet needles, has been prepared.





(I.) (II.) (III.)

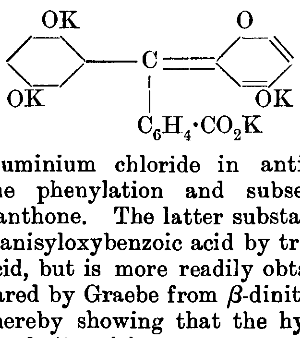
2 : 6 : 2′ : 6′-Tetramethoxydiphenylcarbinol, $CH[C_6H_3(OMe)_2]_2\cdot OH$, is

prepared by Grignard's reaction from 2-iodoresorcinol dimethyl ether and ethyl formate (compare Kauffmann and Franck, Abstr., 1907, i, 1094); it crystallises in colourless, hexagonal prisms, m. p. 179°, and is oxidised by acetic acid and sodium dichromate, yielding 2 : 6 : 2′ : 6′-*tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, which forms colourless, elongated, six-sided plates, m. p. 204°. The latter substance when treated with a solution of aluminium bromide in benzene yields 1 : 8-*dihydroxyxanthone*,

CH:CH——C—O—C——CH:CH
CH:C(OH)·C·CO·C·C(OH):CH

which crystallises in tufts of pale yellow leaflets, m. p. 187°, and interacts with magnesium phenyl bromide, yielding 1 : 8-*dihydroxy-9-phenylxanthen-9-ol*, $C_{19}H_{14}O_4$, which forms elongated, hexagonal, and rhombic plates; the carbinyl *chloride* crystallises in black, opaque needles.

3. *Quinol group.*—Quinolphthalein, unlike *vic.*-orcinolphthalein, does not yield a violet salt when treated with a small quantity of alcoholic potassium hydroxide, probably because the formation of an ortho-quinonoid grouping without fission of the oxygen-bridge is impossible; a violet solution is obtained, however, when a large excess of alkali is employed; it probably contains the *salt* (annexed constitution), and when acidified yields the parent substance.



Quinolbenzein (2 : 7-dihydroxy-9-phenylxanthen-9-ol) may be prepared by hydrolysing 2 : 5 : 2′ : 5′-tetramethoxytriphenylcarbinol with a solution of aluminium chloride in antimony trichloride, or, more readily, by the phenylation and subsequent hydrolysis of 2 : 7-dimethoxyxanthone. The latter substance may be prepared from 5-methoxy-2-*p*-anisyloxybenzoic acid by treatment with hot concentrated sulphuric acid, but is more readily obtained from the dihydroxyxanthone prepared by Graebe from β-dinitroxanthone (compare Abstr., 1890, 504), thereby showing that the hydroxyl groups in this compound occupy the 2 : 7-positions.

2 : 5 : 2′ : 5′-Tetramethoxytriphenylcarbinol may be prepared by the action of benzotrichloride and aluminium chloride on quinol dimethyl ether; it crystallises in colourless plates and prisms, m. p. 125° (compare Kauffmann and Fritz, Abstr., 1909, i, 99).

5-*Methoxy*-p-*anisylsalicylic acid* (5-*methoxy*-2-p-*methoxyphenoxybenzoic acid*), $C_{15}H_{14}O_5$, prepared by the interaction of 2-chloro-5-methoxybenzoic acid and 4-methoxyphenol in the presence of copper powder, crystallises with $\frac{1}{2}H_2O$; the anhydrous substance has m. p. 95°.

2 : 7-Dihydroxyxanthone is best prepared from 2 : 7-diaminoxanthone by warming the diazonium sulphate with 70% sulphuric acid; when treated with methyl sulphate it yields 2 : 7-*dimethoxyxanthone*, $C_{15}H_{12}O_4$, yellow needles, m. p. 180°, which interacts with magnesium phenyl bromide, yielding 2 : 7-*dimethoxy-9-phenylxanthen-9-ol*, $C_{21}H_{18}O_4$, colourless prisms, m. p. 153°. The latter substance, when hydrolysed by aluminium bromide in benzene, yields *quinolbenzein*, the *chloroform* compound of which, $2C_{19}H_{14}O_4,CHCl_3$, forms small, colourless prisms

and decomposes at 100°; the *chloride*, $C_{19}H_{13}O_3Cl$, crystallises in brilliant red prisms or leaflets, and is not readily hydrolysed by water. The black *substance* obtained by heating the chloroform compound at 100° is probably an anhydride of the ortho-quinonoid form of the carbinol, or a mixed anhydride of the carbinol with the ortho-quinonoid form.

4. *Euxanthone group.—Phenyleuxanthenol dimethyl ether* (2 : 8-*dimethoxy-9-phenylxanthen-9-ol*), $C_{21}H_{18}O_4$, results from the interaction of magnesium phenyl bromide and euxanthone dimethyl ether; it crystallises in colourless prisms, m. p. 164—165°, and when treated with aluminium chloride in antimony trichloride yields 9-*chloro*-2 : 8-*dihydroxy-9-phenylxanthen*, $C_{19}H_{13}O_3Cl$, a violet-black, crystalline powder; the corresponding *carbinol* is obtained as a greyish-white, flocculent precipitate by adding acetic acid to a solution of the chloride in an excess of aqueous sodium hydroxide; it could not be obtained in a crystalline form; the carbinol chloride is converted (1) by aqueous ammonia into the corresponding *amide*, $C_{19}H_{15}O_3N$, which crystallises with $1C_5H_5N$ in colourless prisms and turns bluish-black when heated; (2) by an alcoholic solution of sodium ethoxide into the carbinyl *ethyl ether*, $C_{21}H_{18}O_4$, which forms colourless prisms and rhombic plates, m. p. 118—120° (decomp.), and when heated at about 130—140° yields the *anhydride* of the carbinol, $C_{19}H_{12}O_3$, a bluish-black powder.

W. H. G.

Derivatives of Amino-acids. III. Compounds with Cholesterol. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1910, **65**, 69—77. Compare this vol., i, 226).—Chloroacyl chlorides react with cholesterol, yielding chloroacyl derivatives of the alcohol, but it has not been found possible to replace the halogen in these compounds by the amino-group, as ammonia simply hydrolyses the acyl derivatives to cholesterol and the acid amide.

*Cholesteryl α-bromo*iso*valerate*, $CHMe_2 \cdot CHBr \cdot CO \cdot O \cdot C_{27}H_{34}$, crystallises in rhombic plates, sinters at 130°, and has m. p. 134·2—135·2° (corr.).

*Cholesteryl α-bromo*iso*hexoate* crystallises in needles.

Glycylcholesterol hydrochloride, $C_{27}H_{43} \cdot O \cdot CO \cdot CH_2 \cdot NH_2,HCl$, obtained by the action of glycyl chloride hydrochloride on cholesterol in the presence of chloroform, crystallises in slender needles, which decompose at 250°. The free *base*, $C_{27}H_{43} \cdot O \cdot CO \cdot CH_2 \cdot NH_2$, has m. p. 140·5° (corr.), and $[\alpha]_D^{20}$ $-24·98°$ in chloroform solution.

Cholesteryl iso*butyrate*, $CHMe_2 \cdot CO \cdot O \cdot C_{27}H_{43}$, crystallises in plates, has m. p. 125° (corr.), after sintering at 108°, and has $[\alpha]_D^{20}$ $-31·05°$ in chloroform solution.

Cholesteryl iso*valerate*, $CHMe_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{27}H_{43}$, has m. p. 114°, and $[\alpha]_D^{20}$ $-32·7°$. *Cholesteryl laurate*, $C_{11}H_{23} \cdot CO \cdot O \cdot C_{27}H_{43}$, crystallises in slender needles, has m. p. 110°, after sintering at 78°, and $[\alpha]_D^{20}$ $-31·3°$. *Cholesteryl palmitate*, $C_{15}H_{31} \cdot CO \cdot O \cdot C_{27}H_{43}$, has m. p. 78·5—79·5° (corr.) and $[\alpha]_D^{20}$ $-24·2°$, and the *stearate*,

$$C_{17}H_{35} \cdot CO \cdot O \cdot C_{27}H_{43},$$

has m. p. 85—90°

Resorcinol dichloroacetate, $C_6H_4(O\cdot CO\cdot CH_2Cl)_2$, crystallises in four-sided, colourless prisms, m. p. 71·5—72°. *Catechol dichloroacetate* crystallises in brilliant, long, colourless prisms, m. p. 57·5—58°, and *quinol dichloroacetate* in brilliant plates, m. p. 127°. The compounds are hydrolysed by ammonia to the phenol and chloroacetamide. J. J. S.

The Cholesterol Group. VI. Bombicesterol and the Presence of Cholesterol in the Chrysalis of the Silkworm. ANGELO MENOZZI and A. MORESCHI (*Atti R. Accad. Lincei*, 1910, i, 126—129. Compare Abstr., 1908, i, 265).—The authors find that the chrysalis of the silkworm contains two members of the cholesterol group, namely, bombicesterol and ordinary cholesterol, the latter constituting about 13—14% of the mixture. Various hydrocarbons are also present. The following new derivatives of bombicesterol have been prepared.

Dihydrobombicesterol, obtained by passing hydrogen through an ethereal solution of bombicesterol in presence of platinum-black, has m. p. 134°, $[\alpha]_D^{19}$ +19·11°; it gives an *acetyl* derivative, m. p. 128°, $[\alpha]_D^{17}$ +13·45°. T. H. P.

Action of Nascent Hypoiodous Acid on Unsaturated Acids. α-*cyclo*Geranic Acid. J. BOUGAULT (*Compt. rend.*, 1910, **150**, 397—399. Compare Abstr., 1905, i, 9; 1906, i, 848; 1908, i, 179, 269, 537, 983).—When α-*cyclo*geranic acid is dissolved in moist ether and treated with iodine and mercuric oxide, it undergoes oxidation with loss of carbon dioxide. In addition to substances of high boiling point, the product contains Wallach's trimethyl*cyclo*hexenone, $C_9H_{14}O$ (Abstr., 1902, i, 805), together with the corresponding alcohol, 1 : 3 : 3-*trimethyl*-Δ^1-cyclo*hexene*-6-*ol*, $C_8H_{16}O$. The latter was isolated by means of its phthalyl derivative, and obtained as a viscous liquid with a camphoraceous odour, b. p. 193°/760 mm., D_4^{17} 0·9310. The *acetate* has b. p. 206—207°. On oxidation it yields αα-dimethylglutaric acid, the ketone being formed as an intermediate product.

W. O. W.

α-*cyclo*Geranic Acid. J. BOUGAULT (*Compt. rend.*, 1910, **150**, 534—535. Compare preceding abstract).—Mercuric α-*cyclo*geranate decomposes in aqueous solution, liberating carbon dioxide and forming a complex liquid mixture, identical with that obtained by the action of nascent hypoiodous acid on α-*cyclo*geranic acid. When the latter substance is added to a boiling solution of mercuric acetate in acetic acid, a good yield of trimethyl*cyclo*hexenyl acetate is obtained; this is readily hydrolysed, thus affording a convenient method for the preparation of trimethyl*cyclo*hexenol.

Trimethyl*cyclo*hexenone is readily prepared by heating the alcohol on the water-bath, when it rapidly undergoes oxidation. W. O. W.

[Dichlorobenzoic Acids and Substances Derived Therefrom.] FRITZ ULLMANN and CARL WAGNER (*Annalen*, 1910, **371**, 388. Compare Gomberg and Cone, this vol., i, 58).—The dichlorobenzoic acid employed in a recent investigation (compare Abstr., 1907, i, 846) was the 2 : 5- and not the 2 : 4-compound. The compounds obtained from

this acid are consequently 4-chlorodiphenylamine-2-carboxylic acid, 3-chloroacridone, 5-chloro-2-phenoxybenzoic acid, and 2-chloroxanthone.

W. H. G.

Melting-point and Saturation Curves of Binary Systems; Substituted Benzoic Acids and Water. OTTO FLASCHNER and IRVINE GILES RANKIN (*Monatsh.*, 1910, **31**, 23—50. Compare Trans., 1909, **95**, 668).—The solubilities of the hydroxy-, nitro-, amino-, and chloro-benzoic acids, of the toluic acids, and of *p*-bromobenzoic acid, *p*-iodobenzoic acid, *o*-phthalic acid, *p*-methoxybenzoic acid, *o*-acetoxybenzoic acid, and of 1 : 3 : 5-dinitrobenzoic acid in water have been determined by Alexéeff's method (Abstr., 1886, 847) in order to trace the relation between constitution and solubility, and the influence of the critical-solution point on the shape of the m.-p. curve. The results show that the introduction of a hydroxy-, amino-, nitro-, acetyl or carboxyl group into benzoic acid lowers the critical solution temperature, whilst the presence of a methyl or methoxyl group or of a halogen atom causes a rise. The influence of position is not always the same; the hydroxy- and the amino-groups have the greatest lowering effect in the para-, the nitro-group in the ortho-, position. The elevating influence of the methyl group is the same in all three positions, but that of the chlorine atom is greatest in the para-position. A comparison of the critical-solution point with any other property, such as the m. p. or the dissociation constant, shows that a close parallelism does not exist; the nearest agreement is shown in the case of the m. p.'s, the critical solution points and the m. p.'s of substituted benzoic acids containing the same group always changing in the order ortho, meta, para.

C. S.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitroamines. FRÉDÉRIC REVERDIN (*J. pr. Chem.*, 1910, [ii], **81**, 177—183; *Bull. Soc. chim.*, 1910, [iv], **7**, 130—136; *Compt. rend.*, 1910, **150**, 399).—The author gives instances of the reduction of the nitro- to the nitroso-group by concentrated sulphuric acid. Methyl 3 : 5 - dinitro - 4 - nitromethylaminobenzoate, digested with sulphuric acid for twenty-four hours at the ordinary temperature, is converted into methyl 3 : 5-dinitro-4-nitrosomethylaminobenzoate and 3 : 5-dinitro 4-methylaminobenzoate; if the reaction is prolonged for six weeks, the first-mentioned ester and 3 : 5-dinitro-4-methylaminobenzoic acid are formed, the same result being obtained in two and a-half hours, however, at 40—60°. 2 : 4 : 6-Trinitronitromethylaniline yields trinitromethylaniline by heating with concentrated sulphuric acid for many hours on the water-bath. Grimaux and Lefèvre (Abstr., 1891, 1031), by the nitration of dimethyl-*o*-anisidine, obtained, amongst other products, the nitrosoamine and the nitroamine of 3 : 5-dinitromethylanisidine. The nitrosoamine is converted quantitatively into the nitroamine by fuming nitric acid in the cold. The nitroamine is remarkable in that it responds to Liebermann's test; it is converted into the nitrosoamine by concentrated sulphuric acid.

C. S.

Partial Ester Formation of Benzoylaspartic Acid. HERMANN PAULY and JOHN WEIR (*Ber.*, 1910, **43**, 661—670).—Half-esters of

benzoylaspartic acid may be produced either by opening the ring of the anhydride by means of methyl alcohol or by the partial hydrolysis of the normal ester with 1 mol. of alkali. The two methods yield the two isomeric half-esters practically free from admixture with their isomerides. That obtained from the anhydride is the *α-methyl ester-β-acid*, $CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot CO_2H$; it is converted by phosphorus pentachloride into the *β-acid chloride*, and this by ammonia into the *β-amide*, which is identical with the compound obtained from benzoyl-*l*-asparagine by the action of methyl iodide on the silver salt. The half-ester from the normal ester is accordingly the *β-methyl ester-α-acid*, $CO_2H\cdot CH(NHBz)\cdot CH_2\cdot CO_2Me$.

Benzoylaspartic acid is about eight times as strong as succinic acid, whilst the α-ester-β-acid is six times, and the β-ester-α-acid sixteen times, as strong as the half-ester of succinic acid. It is the more strongly acid carboxyl which attracts the methyl group in the splitting of the anhydride and the metal when the normal ester is hydrolysed.

Benzoyl-*l*-aspartic acid has $K = 0.0531$. The anhydride crystallises in asbestos-like needles, m. p. 208—209° (corr.). *α-Methyl β-hydrogen benzoylaspartate* forms minute needles, which sinter at 117—120°, m. p. 123—124°, $K = 0.0186$. The *chloride*, prepared by the action of phosphorus pentachloride on the suspension of the acid in acetyl chloride in the absence of moisture by Fischer's method (Abstr., 1905, i, 863), forms minute needles, m. p. 143—144°. The *amide* forms needles, which sinter at 180°, m. p. 184°, $[\alpha]_D^{20}$, $-14.03°$; prepared by the esterification of benzoylasparagine, it had m. p. 184°, $[\alpha]_D^{20}$ $-13.68°$.

Benzoylasparagine, prepared by benzoylating *l*-asparagine, was obtained as needles, m. p. 190—196°, which contained about 10% of benzoylaspartic acid.

Dimethyl benzoylaspartate, prepared either by the action of methyl iodide on silver benzoylaspartate or by the action of methyl alcohol and dry hydrogen chloride on the acid, forms needles, m. p. 92·5° (corr.).

β-Methyl α-hydrogen benzoylaspartate forms prismatic plates, m. p. 154° (corr.), $K = 0.0500$. It is less soluble than the isomeric acid.

E. F. A.

Preparation of Organic Dithionic Acids (Carbithionic Acids). IGNAZ BLOCH and FRITZ HOHN (D.R.-P. 214888. Compare Abstr., 1906, i, 847; 1907, i, 382, 474).—The dithio-acids of general formula $R\cdot CS_2H$ have usually been prepared by the action of organo-magnesium compounds on carbon disulphide: which method is expensive and not of ready technical application.

It is found that dithio-acids are easily prepared by treating the corresponding aldehyde with hydrogen persulphide in the presence of condensing agents, such as zinc chloride, hydrogen chloride, or sulphuric acid, the reaction being general for both aliphatic and aromatic aldehydes.

Phenylcarbithionic acid (dithiobenzoic acid), $C_6H_5\cdot CS_2H$, is prepared from benzaldehyde, crude hydrogen persulphide, and zinc chloride, the excess of benzaldehyde being removed by steam; the *bismuth* salt is yellow; the *iron* salt, green and soluble in ether; the *methyl* ester, an

oil, b. p. 154—157°/22 mm.; the *ethyl* ester, a red oil, b. p. 165—168°/19 mm.

Thiobenzoyl disulphide, $S_2(CSPh)_2$, forms dark lilac needles, m. p. 117°: Houben (Abstr., 1906, i, 847) gives 92·5°.

Dithiosalicylic acid (o-*hydroxyphenylcarbithionic acid*),

$$HO\cdot C_6H_4\cdot CS\cdot SH,$$

m. p. 46—50°, is more stable, and separates from petroleum in orange-red needles; the *lead* salt crystallises from xylene in orange-red needles; the *methyl* ester is an orange oil of unpleasant odour; the *disulphide*, $S_2(CS\cdot C_6H_4\cdot OH)_2$, m. p. 122·5°, forms brown leaflets with a blue, metallic lustre.

Dithioanisic acid (p-*methoxyphenylcarbithionic acid*),

$$CH_3O\cdot C_6H_4\cdot CS_2H,$$

forms dark rose-coloured, oxidisable crystals; the *lead* salt separates from xylene in orange-yellow needles; the *zinc* salt forms rhombic, yellow crystals; the *mercury* salt, glistening, brown needles; the *bismuth* salt is yellow; the *methyl* ester, m. p. 31°, forms lake-red leaflets; the *ethyl* ester, red crystals; the *disulphide*, $S_2(CS\cdot C_6H_4OMe)_2$, dark red crystals, and has m. p. 163°. These compounds are therapeutically active, and are intermediate products in the colour industry.

F. M. G. M.

Preparation of Dibromophenylglycine-*o*-carboxylic Acid. AKTIENGESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 216266).—Bromophenylglycine-*o*-carboxylic acid has previously been prepared by the action of bromine on phenylglycine-*o*-carboxylic acid in either mineral or acetic acid, or organic solvents. A *dibromophenylglycine-o-carboxylic acid* is produced when phenylglycine-*o*-carboxylic acid (19·5 parts), dissolved in 50% sulphuric acid, is kept at 30° and constantly agitated whilst bromine vapour (32 parts) is introduced with a current of air. The crude product is dissolved in the calculated amount of alkali, reprecipitated with hydrochloric acid, and warmed, when it becomes converted into a colourless, crystalline powder, insoluble in water, but soluble in alcohol or acetic acid, m. p. 227—228° (decomp.). That the bromine has entered the phenyl ring is shown by the non-formation of sodium bromide when the substance is boiled with sodium ethoxide.

F. M. G. M.

Syntheses Effected by Phenylacetonitrile. F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1910, **150**, 531—533).—The sodium derivatives of nitriles of the type $R\cdot CHNa\cdot CN$, prepared by treating the nitriles in ethereal solution with sodamide, readily undergo condensation with alkyl halides; thus ethyl iodide reacts with the sodium derivative of phenylacetonitrile, forming α-phenylbutyronitrile (Neure, Abstr., 1889, 597). *α-Phenyl-β-methylbutyronitrile*,

$$CHPr^{\beta}Ph\cdot CN,$$

has b. p. 245—249°/765 mm.; $D^{15\cdot5}$ 0·967; on hydrolysis it forms *α-phenyl-β-methyl*-n-*butyramide*, $CHPr^{\beta}Ph\cdot CO\cdot NH_2$, silky needles, m. p. 111—112°. *α-Phenyl-γ-methylvaleronitrile*, $C_{12}H_{15}N$, has b. p. 263—266°/765 mm.; D_{16} 0·942. When hydrolysed it yields *α-phenyl-γ-methylvaleric acid*, prisms, m. p. 78—79°.

W. O. W.

Acids of the Phenylpropiolic Series and their Condensation to Naphthalene Derivatives. JOHN E. BUCHER (*J. Amer. Chem. Soc.*, 1910, **32**, 212—221).—A review of work done in connexion with phenylpropiolic acid and its derivatives, with special reference to that of the author and his collaborators (compare Michael and Bucher, Abstr., 1896, i, 85; 1898, i, 256; Bucher, Abstr., 1908, i, 791; Bucher and Slade, this vol., i, 38). E. G.

Preparation of Di- and Tetra-hydro-β-ketonic Acids or their Esters. ARTHUR KÖTZ (D.R.-P. 215424).—When the halogen derivatives of hydroaromatic-β-ketonic-carboxylic acid esters are treated with agents for removing halogen, or distilled under atmospheric pressure, hydrogen halide is eliminated, and unsaturated compounds, many of which are of therapeutic value, are produced. The preparation and properties of 2-bromo*cyclo*hexanone, Δ^2-*cyclo*hexenone and its semicarbazone, and of ethyl-2-hydroxy-$\Delta^{2:6}$-*cyclo*hexadienecarboxylate from ethyl bromo-1-*cyclo*hexanone-2-carboxylate are described (compare Abstr., 1908, i, 173).

Ethyl 4-bromo-1-methyl-3-*cyclo*hexanone-4-carboxylate on distillation yields *ethyl* 1-*methyl*-Δ^3-cyclo*hexen*-5-*one*-4-*carboxylate* (I), a yellow oil, b. p. 110°/15 mm., or its enolic form, *ethyl* 1-*methyl*-$\Delta^{2:4}$-*hexadiene*-3-*ol*-4-*carboxylate* (II), the bromination of which with

$$CH_3\cdot CH<\begin{matrix}CH_2-CO\\CH_2\cdot CH\end{matrix}>C\cdot CO_2Et \quad \text{(I.)}$$

$$CH_3\cdot CH<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CBr\cdot CO_2Et \begin{matrix}\nearrow\\ \searrow\end{matrix}$$

$$CH_3\cdot CH<\begin{matrix}CH{:}C(OH)\\CH_2-CH\end{matrix}>C\cdot CO_2Et \quad \text{(II.)}$$

2 atoms of bromine in carbon disulphide solution leads to the formation of ethyl 4 : 5-dibromo-1-methyl-Δ^2-*cyclo*hexene-3-ol-4-carboxylate (III); this on distillation gives *ethyl bromo*-1-*methyl*-Δ^{25}-cyclo*hexadiene*-3-*ol*-4-*carboxylate* (IV), a pale yellow oil, b. p. 161°/13 mm.:

$$CH_3\cdot CH<\begin{matrix}CH{:}C(OH)\\CH_2\cdot CHBr\end{matrix}>CBr\cdot CO_2Et \quad \text{(III.)}$$

$$CH_3\cdot CH<\begin{matrix}CH{:}C(OH)\\CH=CH\end{matrix}>CBr\cdot CO_2Et. \quad \text{(IV.)}$$

F. M. G. M.

Preparation of α-Monohalogen-substitution Products of Hydroaromatic-β-ketonic-carboxylic Esters. ARTHUR KÖTZ (D.R.-P. 215423).—The α-halogen-substitution products of hydroaromatic-β-ketonic carboxylic esters can be obtained by the direct halogenation of these substances.

Ethyl 1-*chloro*-2-cyclo*hexanone*-1-*carboxylate*,

$$CH_2<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CCl\cdot CO_2Et,$$

b. p. 138—139°/13 mm., an oily fluid with penetrating odour, is

obtained when ethyl 2-*cyclo*hexanone-1-carboxylate is cooled and treated with dry chlorine; hydrogen chloride is removed by a current of dry carbon dioxide, and the product distilled under reduced pressure.

Ethyl 1-*bromo*-2-cyclo*hexanone*-1-*carboxylate* is similarly prepared by employing bromine instead of chlorine, as in the previous experiment; it is a pale yellow oil with unpleasant odour, and has b. p. 144°/13 mm.

Ethyl 4-*chloro*-1-*methyl*-3-cyclo*hexanone*-4-*carboxylate*,

$$CH_3\cdot CH<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CCl\cdot CO_2Et,$$

b. p. 138°/11 mm., is obtained from ethyl 1-methyl-3-*cyclo*hexanone-4-carboxylate, but the action proceeds with less violence.

Ethyl 1-*bromo*-1-*methyl*-3-cyclo*hexanone*-4-*carboxylate*, b. p. 149—150°/12 mm., has similar properties, but in this case the reaction does not proceed readily unless hydrogen bromide is expelled by shaking during the experiment. F. M. G. M.

Some Derivatives of Salicylic Acid. ALFRED EINHORN and ALEXANDER VON BAGH (*Ber.*, 1910, **43**, 322—336).—o-4-*Nitrobenzoyloxybenzoic acid*, $CO_2H\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, m. p. 205°, is a yellow, crystalline powder obtained by adding a benzene solution of *p*-nitrobenzoyl chloride to a well cooled solution of salicylic acid and dimethylaniline in the same solvent. The *ethyl* ester,

$$CO_2Et\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_4\cdot NO_2,$$

m. p. 107—108°, prepared from ethyl salicylate and *p*-nitrobenzoyl chloride in pyridine, is reduced by stannous chloride and alcoholic hydrogen chloride to *ethyl* o-4-*aminobenzoyloxybenzoate*, m. p. 109—110°. *Ethyl* o-4-*dimethylaminobenzoyloxybenzoate*, m. p. 106°, is obtained by heating ethyl salicylate and *p*-dimethylaminobenzoic anhydride for ten hours at 180—200°. The *chlorocarbonate* of methyl salicylate, $CO_2Me\cdot C_6H_4\cdot O\cdot COCl$, m. p. 24°, b. p. 141—142°/0 mm., is ultimately obtained when a cooled 20% benzene solution of carbonyl chloride is slowly added to methyl salicylate and quinoline dissolved in benzene; its ethereal solution yields with ethereal ammonia the *carbamate*, $CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot NH_2$, m. p. 145°, and with ethereal diethylamine the *diethylcarbamate*, b. p. 182°/0 mm. The passing of hydrogen chloride into a well-cooled suspension of the carbamate in 40% formaldehyde leads to the formation of the *dichlorodimethylcarbamate*,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot N(CH_2Cl)_2,$$

m. p. 75—76°, a cold ethereal solution of which reacts with piperidine to form methyl salicylate, formaldehyde, and *α-piperidyl-β-*(1)*-piperidylmethylcarbamide*, $C_5NH_{10}\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, m. p. 142—143°.

o-*Carbomethoxyphenyl* m-*carbethoxyphenylcarbamate*,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Et,$$

m. p. 123°, is obtained by slowly mixing cold ethereal solutions of the chlorocarbonate of methyl salicylate and ethyl *m*-aminobenzoate. The corresponding *para*-compound, m. p. 153—154°, prepared in a similar manner, loses methyl alcohol after some hours at 130—140°, and

yields the *ethyl carbonylsalicyl*-p-*aminobenzoate*, m. p. 185—187° described below.

o-*Ethylcarbonatobenzoyl chloride*, $COCl\cdot C_6H_4\cdot O\cdot CO_2Et$, b. p. 155—165°/20—25 mm., obtained by the action of phosphorus pentachloride on *o*-ethylcarbonatobenzoic acid (Abstr., 1909, i, 161) in chloroform, reacts with methyl anthranilate in cold pyridine to form *methyl* o-*ethylcarbonatobenzoylanthranilate*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Me,$$

m. p. 113°, which loses ethyl alcohol at 230°, forming *methyl carbonylsalicyl*-o-*aminobenzoate*, $CO_2Me\cdot C_6H_4\cdot N{<}{\begin{smallmatrix}CO\cdot O\\ CO\text{—}\end{smallmatrix}}{>}C_6H_4$, m. p. 145°. *o*-Ethylcarbonatobenzoyl chloride reacts with ethyl *m*-aminobenzoate in cold pyridine directly to form *ethyl carbonylsalicyl*-m-*aminobenzoate*, m. p. 185—186°, and similarly with ethyl *p*-aminobenzoate to form *ethyl carbonylsalicyl*-p-*aminobenzoate*, m. p. 185—187°. *Ethyl* o-*ethylcarbonatobenzoyl*-p-*aminobenzoate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot O\cdot CO_2Et$, m. p. 90—92°, is obtained, however, when an ethereal solution of ethyl *p*-aminobenzoate is treated with *o*-ethyl carbonatobenzoyl chloride at 0°; it is converted into the preceding compound at 160—200°. o-*Ethylcarbonatobenzoic anhydride*, $O(CO\cdot C_6H_4\cdot O\cdot CO_2Et)_2$, m. p. 62—64°, is obtained from salicylic acid diethyl dicarbonate (D.R.-P. 117267) by prolonged keeping, and is converted by cold concentrated ammonium hydroxide into *carbonylsalicylamide*, m. p. 227°. C. S.

Colourless and Yellow Thiosalicylic [*o*-Thiolbenzoic] Acids. OSCAR HINSBERG (*Ber.*, 1910, **43**, 651—654).—*o*-Thiolbenzoic acid, $SH\cdot C_6H_4\cdot CO_2H$, exists in a colourless as well as in the ordinary yellow modification, whereas its methyl and acetyl derivatives have been obtained in colourless modifications only. Other thiophenols also exist in two modifications (Abstr., 1906, i, 654).

a-*o*-Thiolbenzoic acid, obtained by treating the crude acid or dithiosalicylic acid (m. p. 289°) with glacial acetic acid, tin, and concentrated hydrochloric acid until all is dissolved, crystallises in colourless prisms, m. p. 164—165°. It is less soluble than the yellow isomeride, from which it is obtained by treatment with stannous chloride and glacial acetic acid or by heating at 200°. The yellow isomeride, *β*-*o*-thiolbenzoic acid, has m. p. 163—164°, after softening at 158°.

The *methyl ether*, $SMe\cdot C_6H_4\cdot CO_2H$, crystallises in long, colourless needles, m. p. 169°, and undergoes no alteration when heated to 250°. o-*Acetylthiolbenzoic acid*, $SAc\cdot C_6H_4\cdot CO_2H$, crystallises in colourless needles, m. p. 125°, and when hydrolysed with hydrochloric acid yields *a*-*o*-thiolbenzoic acid. J. J. S.

Derivatives of Thiosalicylic [*o*-Thiolbenzoic] Acid and of Thioxanthone. FRITZ MAYER (*Ber.*, 1910, **43**, 584—596. Compare Abstr., 1909, i, 405, 823).—Methyl, carboxy-, polynitro-, and chloronitro-derivatives of thiosalicylic [*o*-thiolbenzoic] acid have been prepared, mainly by heating substituted benzoic acids with thiosalicylic acid and copper powder under pressure.

The products can be oxidised in much the same manner as the compounds already described, but it is found that 2 : 2′-thiodibenzoic acid,

like other ortho-compounds, is completely destroyed by chromic acid; the ester, on the other hand, is readily oxidised to a sulphoxide ester. Dinitro-2 : 2′-thiodibenzoic acid is only slowly oxidised by chromic anhydride in acetic acid solution, and the *s*-trinitro-derivative is extremely resistant to oxidising agents (Blanksma, *Rec. trav. chim.*, 1901, 20, 426).

Most of the sulphides can be transformed into thioxanthones by means of sulphuric acid. The dinitro-derivative does not yield a thioxanthone by this method, but the corresponding amino-compound does. When the acid chloride of dinitrothiodibenzoic acid is heated with aluminium chloride and nitrobenzene, it yields 2 : 4-dinitrothioxanthone, but with benzene and aluminium chloride yields 2 : 4-dinitro-2′-benzoyldiphenyl sulphide.

The thioxanthonecarboxylic acids readily loses carbon dioxide, yielding thioxanthones.

4-Methyl-2′-carboxydiphenyl sulphide [2 : 2′-thio-4-methyldibenzoic acid] (compare Goldberg, Abstr., 1905, i, 59) can be prepared by condensing *o*-diazobenzoic acid with an alkaline solution of *p*-thiocresol.

The corresponding *sulphoxide*, $C_6H_4Me\cdot SO\cdot C_6H_4\cdot CO_2H$, crystallises in colourless needles, and has m. p. 244°, after softening at 236°. 2-*Methylthioxanthone*, $C_6H_4<\substack{S\\CO}>C_6H_3Me$, crystallises in yellow needles, m. p. 123°, and when oxidised with chromic anhydride yields 2-methylbenzophenonesulphone (Ullmann and Lehner, Abstr., 1905, i, 290).

2 : 2′-*Dicarboxydiphenyl sulphide* [2 : 2′-*thiodibenzoic acid*],

$$S(C_6H_4\cdot CO_2H)_2,$$

obtained by heating thiosalicylic acid, *o*-chlorobenzoic acid, copper powder, potassium carbonate, and water at 135—140° for three hours, crystallises in colourless needles, m. p. 229—230°. The *methyl* ester, $C_{16}H_{14}O_4S$, has m. p. 84°, and the *ethyl* ester, $C_{18}H_{18}O_4S$, m. p. 57—58°.

2 : 2′-*Dicarboxydiphenyl sulphoxide* [*sulphonyldibenzoic acid*],

$$O:S(C_6H_4\cdot CO_2H)_2,$$

is best obtained by hydrolysis of its esters, and crystallises in well developed, colourless prisms, m. p. 312°. The *methyl* ester, $C_{16}H_{14}O_5S$, crystallises in brilliant plates, m. p. 156°, and the *ethyl* ester,

$$C_{18}H_{18}O_5S,$$

in compact needles, m. p. 107—108°. 2 : 2′-*Dicarboxydiphenylsulphone*, $SO_2(C_6H_4\cdot CO_2H)_2$, obtained by oxidising the sulphide with permanganate, crystallises in felted needles, m. p. 138—139°. *Thioxanthone-4-carboxylic acid*, $C_6H_4<\substack{S\\CO}>C_6H_3\cdot CO_2H$, forms yellow, microscopic crystals, m. p. 336—337°. The *methyl* ester, $C_{15}H_{10}O_3S$, has m. p. 191°, and the *amide*, $C_{14}H_9O_2NS$, forms pale yellow needles, m. p. 286°.

o-2′ : 4′-*Dinitrophenylthiolbenzoic acid*, $C_6H_3(NO_2)_2\cdot S\cdot C_6H_4\cdot CO_2H$, obtained from 1-chloro-2 : 4-dinitrobenzene, forms yellow crystals, m. p. 179—180°; the *methyl* ester has m. p. 117—117·5°; the *sulphoxide*, $C_{13}H_8O_7N_2S$, forms compact, pale greenish-yellow crystals, m. p. 239—240°, and yields a *methyl* ester, $C_{14}H_{10}O_7N_2S$, m. p. 171—172°;

the *sulphone*, $C_{13}H_8O_8N_2S$, forms colourless crystals, m. p. 215—217°; 2 : 4-*dinitro-2′-benzoyldiphenyl sulphide*, $C_6H_3(NO_2)_2{\cdot}S{\cdot}C_6H_4{\cdot}COPh$, has m. p. 155—156°, and the corresponding *toluoyl* derivative,

$$(NO_2)_2C_6H_3{\cdot}S{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Me,$$

has m. p. 122°. 2 : 4-*Dinitrothioxanthone*, $C_6H_4<\genfrac{}{}{0pt}{}{S}{CO}>C_6H_2(NO_2)_2$, forms greenish-yellow needles with a metallic lustre, and has m. p. 225—226°.

o-2′ : 4′ : 6′-*Trinitrophenylthiolbenzoic acid*, $(NO_2)_3C_6H_2{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$, obtained from picryl chloride, forms yellow crystals, m. p. 240—241°. The *methyl* ester forms brilliant, reddish-yellow needles, m. p. 181·5°.

o-4′-*Chloro-2′-nitrophenylthiolbenzoic acid*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

has m. p. 155—156·5°, and 2-*chloro-4-nitrothioxanthone*,

$$C_6H_4<\genfrac{}{}{0pt}{}{S}{CO}>C_6H_2Cl{\cdot}NO_2,$$

forms slender, yellow needles, m. p. 219—220°.

o-5-*Chloro-2-nitrophenylthiolbenzoic acid*, $C_{13}H_8O_4NClS$, obtained from 1-chloro-3 : 4-dinitrobenzene, has m. p. 188—189°, and 1-*chloro-4-nitrothioxanthone*, $C_{13}H_6O_3NClS$, m. p. 204—205°. J. J. S.

Action of Sulphosalicylic Acid on Trisodium Phosphate. LÉONCE BARTHE (*Compt. rend.*, 1910, **150**, 401—403. Compare Abstr., 1908, i, 271).—*Sodium oxyphosphodisulphosalicylate*,

$$PO[O{\cdot}C_6H_3(SO_3H){\cdot}CO_2Na]_2{\cdot}ONa,$$

is obtained in the form of brilliant prisms containing $2H_2O$ when a boiling aqueous solution of trisodium phosphate is mixed with an alcoholic solution of sulphosalicylic acid. The compound is a dibasic acid; it gives a red coloration with Millon's reagent, and a bluish-violet colour with ferric chloride.

By the interaction of trisodium arsenate and sulphosalicylic acid, a *compound* has been obtained, the composition of which appears to agree with the formula $AsO[O{\cdot}C_6H_3(SO_3H){\cdot}CO_2Na]_3$.

W. O. W.

Preparation of *o*- and *peri*-Thiophenolcarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216269).—*o*- or *peri*-Cyanoarylsulphinic acids are obtained in the form of their zinc salts by the slow reduction at the ordinary temperature of cyanoarylsulphonyl chlorides with zinc dust and water; the free acids are colourless powders, sparingly soluble in water, without characteristic melting point, and readily undergo atmospheric oxidation to the corresponding sulphonic acids. The zinc salts are somewhat sparingly soluble in water. When the preceding reduction mixture is treated with sulphuric acid and a further quantity of zinc, and the action allowed to proceed during several days until the evolution of nitrogen ceases, the corresponding zinc thiophenolcarboxylates are precipitated, the hydrolysis of the nitrile group having taken place simultaneously with the reduction of the sulphinic group. These acids are colourless, crystalline powders, soluble in alkali carbonates, yielding characteristic colours with concentrated sulphuric acid, and are readily oxidised to the corresponding dithio-acids.

5-Chloro-3-thiol-*o*-toluic acid, $SH\cdot C_6H_2MeCl\cdot CO_2H$, m. p. about 235°, is prepared by treating diazotised 5-chloro-*o*-toluidine-3-sulphinic acid with cuprous cyanide, and the 2-cyanotoluene-3-sulphinic acid then formed, with phosphorus pentachloride, and subsequently reducing first with zinc dust in acetone solution, and, finally, in the presence of sulphuric acid; it forms colourless needles, yields a blue coloration with concentrated sulphuric acid, and is readily oxidised to dithiochlorotoluic acid. The following compounds are mentioned in the patent:

3-*Thiol*-p-*toluic acid*, $SH\cdot C_6H_3Me\cdot CO_2H$, prepared from the corresponding cyanotoluenesulphinic acid.

6-*Thiol*-2 : 4-*dimethylbenzoic acid*, $SH\cdot C_6H_2Me_2\cdot CO_2H$, from cyanoxylenesulphinic acid.

2-*Thiolnaphthalene*-1-*carboxylic acid*, $SH\cdot C_{10}H_6\cdot CO_2H$, from 1-cyanonaphthalene-2-sulphinic acid; and 8-*thiolnaphthalene*-1-*carboxylic acid*, from the corresponding 1 : 8-cyanosulphinic acid.

F. M. G. M.

Methyl Anisoylacetates. ANDRÉ WAHL and C. SILBERZWEIG (*Compt. rend.*, 1910, **150**, 538—540. Compare Abstr., 1908, i, 647).—The three methyl anisoylacetates have been prepared by condensing methyl acetate with *o*-, *m*-, and *p*-methoxybenzoic acids in presence of sodium.

Methyl o-*anisoylacetate*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Me$, is a pale yellow liquid boiling at 179—180°/15 mm., with formation of small quantities of o-*anisoyldehydracetic acid*, occurring in yellow crystals, m. p. 214—215°. The green *copper* salt, $(C_{10}H_{11}O_4)_2Cu$, has m. p. 170—172°; a solution in methyl alcohol deposits, on boiling, blue crystals of a basic salt, $C_{12}H_{14}O_5Cu$ (compare Wislicenus, Abstr., 1899, i, 192). The following derivatives of the new ester are described: the *nitroso*-derivative, m. p. 145—147°; o-*anisoylphenylpyrazolone*, m. p. 133—134°; o-*anisoyl*-p-*nitrophenylpyrazolone*, m. p. 217—218°; *methyl benzeneazo*-o-*anisoylacetate*, m. p. 138—139°.

Methyl m-*anisoylacetate* is an amber-coloured liquid, b. p. 180°/14 mm., forming a green *copper* salt, m. p. 172—173°, and a *nitroso*-derivative, m. p. 115—116°. m-*Anisoyldehydracetic acid* occurs in yellow crystals, m. p. 185°. m-*Anisoylphenylpyrazolone* has m. p. 124°; *methyl benzeneazo*-m-*anisoylacetate* has m. p. 72—73°.

Methyl p-*anisoylacetate* forms pale yellow crystals, m. p. 27—28°, b. p. 190—192°/10 mm. The *copper* salt has m. p. 248—250°, and the *nitroso*-derivative, m. p. 154°. p-*Anisoyldehydracetic acid* has m. p. 190°; p-*anisoylphenylpyrazolone* has m. p. 136—137°. *Methyl benzeneazo*-p-*anisoylacetate*, m. p. 121—122°, forms an *acetyl* derivative, m. p. 111—113°; as this yields acetanilide on reduction, it would appear to be an acetylhydrazone (compare Schoonjans, Abstr., 1898, i, 425).

W. O. W.

Action of Amines on Phthalic Acid. VI. J. BISHOP TINGLE an B. F. PARLETT BRENTON (*J. Amer. Chem. Soc.*, 1910, **32**, 113—117).—A study has been made of the action of phthalic anhydride on several amino-compounds. With camphylamine, *phthalylcamphylimide*,

$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot C_{10}H_7$, m. p. 54°, is produced. In the case of benzidine, an insoluble compound is obtained, which does not melt below 300°. *m*-Aminobenzoic acid yields phthalyl-*m*-aminobenzoic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$ (compare Gabriel, Abstr., 1879, 323, and Piutti, Abstr., 1883, 999).

Acetanilide, aceto-*p*-toluidide, and formo-β-naphthalide react with phthalic anhydride with the replacement of the acetyl or formyl group by the phthalyl group, phthalyl-β-naphthylimide, for example, being produced from formo-β-naphthalide. Carbamide, methylcarbamide, ethylcarbamide, benzylcarbamide, and phenylcarbamide are converted into phthalimide, methylphthalimide, ethylphthalimide, benzylphthalimide, and phenylphthalimide respectively, ammonia and carbon dioxide being evolved in each case. Phenylthiocarbamide behaves in the same way as phenylcarbamide, except that carbonyl sulphide is evolved instead of carbon dioxide. E. G.

Action of Unsaturated Dicarboxylic Acids on *p*-Aminophenols. ARNALDO PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 315—318).—A résumé is given of the work of the author and his assistants on the amic acids, imides, and diamides derived from the actions of maleic, fumaric, citraconic, mesaconic, itaconic, pyrocinchonic, phthalic, and camphoric acids on various *p*-aminophenols (compare this vol., i, 22). The cases of chromo-isomerism and of true chemical isomerism observed with these compounds are indicated.

T. H. P.

New Synthesis of 4:4′-Dimethylpyranthrone. ROLAND SCHOLL, KURT LIESE, KARL MICHELSON, and ERNST GRUNEWALD (*Ber.*, 1910, **43**, 512—518. Compare this vol., i, 271).—The reaction in carbon disulphide between 2 : 4 : 2′ : 4′-tetramethyl-1 : 1′-diphenyl, phthalic anhydride, and aluminium chloride leads to the formation of a tarry product containing at least three substances. The residue left by treating the product with a large volume of cold benzene is crystallised from chloroform, and consists of 2 : 4 : 2′: 4′-*tetramethyldiphenyl*-5:5′-*diphthaloylic acid*, $C_{12}H_4Me_4(CO\cdot C_6H_4\cdot CO_2H)_2$, m. p. 242°, the constitution of which is proved by its conversion by concentrated sulphuric acid into 2 : 4 · 2′ : 4′-tetramethyl-1 : 1′-dianthraquinoyl, which in turn was converted into 4 : 4′-dimethylpyranthrone. The benzene extract of the tarry product is evaporated, and the residue is separated by ether and by cold chloroform into two substances, the one soluble, the other insoluble. The latter is recrystallised from nitrobenzene, and consists probably of 2 : 4 : 2′ : 4′-*tetramethyldiphenyl*-3 : 3′-*diphthaloylic acid*, m. p. 320°, since it is converted by concentrated sulphuric acid, not into an anthraquinone derivative, but into a *disulphonic acid*, $C_{32}H_{26}O_{12}S_2$. The soluble substance has not been obtained pure. It has m. p. 92—94°, and appears to have the composition $C_{32}H_{24}O_5$; it is not an anthraquinone derivative, and is not converted into one by concentrated sulphuric acid at 120°, is soluble in dilute alkali, and is provisionally regarded as 2 : 4 : 2′ : 4′-*tetramethyl*-5 : 5′-*phthaloyldiphenyl*-3-*phthaloylic acid*.

C. S.

Constitution of Tannin. VII. MAXIMILIAN NIERENSTEIN (*Ber.*, 1910, **43**, 628—634. Compare Abstr., 1906, i, 446; 1907, i, 331; 1908, i, 80, 897; 1909, i, 402, 948).—The following facts are brought forward in favour of the view that pure tannin is a mixture of a digallic acid and leucotannin. By repeated conversion into its ethyl carbonato-derivative and hydrolysis of this with pyridine (Fischer, Abstr., 1908, i, 892), it has been found possible to isolate digallic acid in a crystalline, optically inactive form.

d-l-Hexa-acetyl-leucotannin can be obtained by the reduction of penta-acetyldigallic acid with zinc dust and acetic acid in the presence of acetic anhydride, and is readily resolved into its optically active components by means of strychnine. Both acetyl compounds can be hydrolysed by means of sodium carbonate solution saturated with carbon dioxide.

The view that the activity of tannin is due to the leucotannin and not to the presence of a sugar (Abstr., 1909, i, 174) is still held.

Digallic acid, $C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$, crystallises with $2H_2O$, which it loses at 110°, and then has m. p. 268—270°, after sintering at 214°. It is inactive, and when oxidised with hydrogen peroxide yields luteoic and ellagic acids (Abstr., 1908, i, 897). The *penta-acetyl* derivative, $C_{24}H_{20}O_{14}$, crystallises in slender needles, m. p. 211—214°, and the *pentabenzoyl* derivative, $C_{49}H_{30}O_{14}$, has m. p. 187—189°. The *pentaethylcarbonato*-compound,

$$C_6H_2(O\cdot CO_2Et)_3\cdot CO\cdot O\cdot C_6H_2(O\cdot CO_2Et)_2\cdot CO_2H,$$

crystallises in small cubes, m. p. 194—195°.

d-l-*Hexa-acetyl-leucotannin*,

$$C_6H_2(OAc)_3\cdot CH(OAc)\cdot O\cdot C_6H_2(OAc)_2\cdot CO_2H,$$

also crystallises in small cubes, m. p. 154—155°.

Strychnine l-*hexa-acetyl-leucotannin* is less soluble than the *d*-salt, and *l*-hexa-acetyl-leucotannin itself crystallises in minute needles containing $1H_2O$ and having m. p. 151° and $[\alpha]_D^{15}$ $-46°$. The *d*-compound has m. p. 153—154° and $[\alpha]_D^{20}$ $+121\cdot5°$.

The digallic acid is not identical with Fischer's acid. J. J. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. IV. EMIL FISCHER and KARL FREUDENBERG (*Annalen*, 1910, **372**, 32—68. Compare Fischer, Abstr., 1908, i, 892; 1909, i, 161, 309).—The present communication contains a description of the syntheses of many complex substances which have been effected by coupling the sodium salts of phenolcarboxylic acids with the chlorides of methylcarbonato-carboxylic acids; for example, *p*-ethylcarbonatobenzoyl-*p*-oxybenzoyl chloride reacts with sodium *p*-hydroxybenzoyl-*p*-oxybenzoate, yielding the ethylcarbonato-derivative of tri-*p*-oxybenzoyl-*p*-oxybenzoic acid,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

which when hydrolysed cautiously yields the corresponding phenolcarboxylic acid; di-*p*-oxybenzoyl-*p*-oxybenzoic acid,

$$OH\cdot[C_6H_4\cdot CO\cdot O\cdot]_2\cdot C_6H_4\cdot CO_2H,$$

is similarly prepared from *p*-ethylcarbonatobenzoyl chloride and *p*-hydroxybenzoyl-*p*-oxybenzoic acid. It will no doubt be possible to prepare, by similar means, a large number of analogous substances from

other hydroxybenzoic acids, and since many undoubtedly occur in nature, as, for example, tannin, it is considered advisable to classify them under the collective name *depside* (δέψειν tan), and, as in the case of the polysaccharides and polypeptides, to distinguish between di-, tri-, tetra-depsides, etc., according to the number of phenolcarboxylic acid residues contained in the molecule.

The preparation and properties of vanilloylvanillin and vanilloylglycine are described, likewise a method whereby a 45% yield of *p*-hydroxybenzoyloxybenzoic acid may be obtained by acting on an ethereal solution of *p*-hydroxybenzoic acid with phosphoryl chloride.

p-*Ethylcarbonatobenzoic acid*, $CO_2Et \cdot O \cdot C_6H_4 \cdot CO_2H$, prepared from *p*-hydroxybenzoic acid and ethyl chlorocarbonate, crystallises in long, colourless needles, m. p. 156—157° (corr.); the *chloride*, $C_{10}H_9O_4Cl$, has m. p. 41°, b. p. 170°/12 mm. The latter substance interacts with *p*-hydroxybenzoyl-*p*-oxybenzoic acid in an aqueous solution of sodium hydroxide, yielding *ethylcarbonatodi*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$C_{24}H_{18}O_9,$$

which crystallises from amyl alcohol in aggregates of colourless leaflets and from pyridine in small, slender needles, m. p. 243—244° (corr., decomp.), and when hydrolysed cautiously yields *di*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{21}H_{14}O_7$, which crystallises in long, colourless needles, commences to decompose at 283° (corr.), fuses at 300° (corr.), and is probably identical with the compound obtained by Klepl by strongly heating *p*-hydroxybenzoic acid (compare Abstr., 1884, 446).

p-*Ethylcarbonatobenzoyloxybenzoic acid*, $C_{17}H_{14}O_7$, obtained by the action of *p*-ethylcarbonatobenzoyl chloride on *p*-hydroxybenzoic acid, crystallises in colourless leaflets, m. p. 112° (corr.); the *chloride*, $C_{17}H_{13}O_6Cl$, crystallises in small, slender needles, m. p. 113° (corr.), and couples with *p*-hydroxybenzoyloxybenzoic acid, yielding *ethylcarbonatotri*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{31}H_{22}O_{11}$, which crystallises from acetylene tetrachloride in stellate aggregates of microscopic, slender leaflets, m. p. 275° (corr., decomp.), and on partial hydrolysis yields *tri*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$OH \cdot [C_6H_4 \cdot CO \cdot O \cdot]_3C_6H_4 \cdot CO_2H,$$

crystallising from ethyl oxalate in microscopic, colourless, silky needles, m. p. 325° (corr., decomp.); the tetradepside is extremely insoluble in organic solvents, and is not identical with Schiff's tetra-*p*-oxybenzoid (compare Abstr., 1883, 335).

4-*Methylcarbonato*-3-*methoxybenzoic acid*,

$$CO_2Me \cdot O \cdot C_6H_3(OMe) \cdot CO_2H,$$

is prepared by the interaction of vanillic acid and methyl chlorocarbonate in a *N*-sodium hydroxide solution; it crystallises in small, colourless needles, m. p. 159° (corr., decomp.), and may be sublimed in a current of carbon dioxide at 145—150°; it does not give a coloration with ferric chloride, although, contrary to Tiemann's statement (compare Abstr., 1875, 1198), vanillic acid gives an intense reddish-brown coloration; the *chloride*, $C_{10}H_9O_5Cl$, crystallises in small, colourless needles, m. p. 79°, b. p. 180°(corr.)/11 mm., and interacts (1) with *p*-hydroxybenzoic acid, yielding 4-*methylcarbonato*-3-*methoxybenzoyl*-p-*oxybenzoic acid*, $CO_2Me \cdot O \cdot C_6H_3(OMe) \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$, colourless, microscopic leaflets, m. p. 219° (corr., decomp.), which is hydrolysed

by a cold *N*-solution of ammonium hydroxide, yielding *vanilloyl*-p-*oxybenzoic acid*, $OH\cdot C_6H_3(OMe)\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, small needles, prisms, and leaflets, m. p. 227° (corr.); (2) with *p*-hydroxybenzoyloxybenzoic acid, yielding *4-methylcarbonato-3-methoxybenzoyl*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{24}H_{18}O_{10}$, glistening, slender leaflets and needles, m. p. 244—246° (corr.), the *chloride* of which, $C_{24}H_{17}OCl$, crystallises in microscopic leaflets, m. p. 170—171 (corr.); the former compound when hydrolysed yields *vanilloyl*-p-*oxybenzoyl*-p-*oxybenzoic acid*, $C_{22}H_{16}O_8$, m. p. 241° (corr.), crystallising with 1MeOH in long, slender prisms; (3) with vanillin, yielding *4-methylcarbonato-3-methoxybenzoylvanillin*, $C_{18}H_{16}O_8$, and is converted by a dilute aqueous methyl-alcoholic solution of sodium hydroxide into *vanilloylvanillin*,

$$OH\cdot C_6H_3(OMe)\cdot CO_2\cdot C_6H_3(OMe)\cdot CHO,$$

crystallising in tufts of colourless, glistening needles, m. p. 140—141° (corr.), the sodium hydrogen sulphite *compound* of which forms slender, colourless needles; (4) with ethyl aminoacetate, yielding *ethyl 4-methylcarbonato-3-methoxybenzoylaminoacetate*, $C_{14}H_{17}O_7N$, which crystallises in glistening, four-sided leaflets, m. p. 93—94° (corr.), and on hydrolysis yields *vanilloylglycine*, $OH\cdot C_6H_3(OMe)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, short, microscopic prisms, m. p. 167°; the latter substance crystallises with H_2O in large, colourless leaflets, which sinter at about 75°; it has both an acid and bitter taste.

4-Methylcarbonato-3-methoxybenzoyl-p-*oxybenzoyl chloride*, $C_{17}H_{13}O_7Cl$, crystallises in microscopic leaflets and needles, m p. 128—129° (corr.), and reacts with *p*-hydroxybenzoyloxybenzoic acid, yielding *4-methylcarbonato-3-methoxybenzoyldi*-p-*oxybenzoyl*-p-*oxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CO_2\cdot[C_6H_4\cdot CO\cdot O\cdot]_2C_6H_4\cdot CO_2H,$$

which crystallises in stellate groups of small leaflets, m. p. 272° (corr., decomp.), and when hydrolysed yields *vanilloyldi*-p-*oxybenzoyl*-p-*oxybenzoic acid*, crystallising in small needles and microscopic, spear-shaped plates, m. p. 254° (corr., decomp.).

4-Methylcarbonato-3-methoxybenzaldehyde, $C_{10}H_{10}O_5$, prepared from vanillin and methyl chlorocarbonate, forms colourless needles, m. p. 89° (corr.); it yields the corresponding acid when oxidised with potassium permanganate, which readily passes into vanillic acid. W. H. G.

Photochemistry of *o*-Nitrated Benzaldehydes. EUGEN BAMBERGER and FRANZ ELGAR (*Annalen*, 1910, **371**, 319—365).—The formation of ethyl *o*-nitrosobenzoate by the action of light on an ethyl-alcoholic solution of *o*-nitrobenzaldehyde (compare Ciamician and Silber, Abstr., 1901, i, 390; 1902, i, 433) is shown to take place in the following stages: $NO_2\cdot C_6H_4\cdot CHO \xrightarrow{Et\cdot OH} NO_2\cdot C_6H_4\cdot CH(OEt)_2 \longrightarrow [NO\cdot C_6H_4\cdot C(OEt)_2\cdot OH] \longrightarrow NO\cdot C_6H_4\cdot CO_2Et + Et\cdot OH$; it has been found possible to isolate the *o*-nitrobenzaldehydediethylacetal formed in this way. A second reaction takes place simultaneously, namely, the formation of 2:2′-azoxybenzoic acid by way of *o*-nitrosobenzoic acid. Methyl alcohol, propyl alcohol, *iso*propyl alcohol, and *iso*butyl alcohol react in the same way as ethyl alcohol; in the case of *iso*propyl alcohol, however, only a very small quantity of *iso*propyl *o*-nitrosobenzoate is formed, the chief product being *o*-nitrosobenzoic acid; this is found to be due to the slow rate with which the *iso*propyl-

acetal of *o*-nitrobenzaldehyde is formed, for the latter substance decomposes into *iso*propyl *o*-nitrosobenzoate and *iso*propyl alcohol under the influence of light with almost the same readiness with which the other acetals undergo the analogous transformation.

Quantitative experiments carried out with the alcohols mentioned show that the rate with which the acetal is formed, either through the agency of sunlight or by using hydrogen chloride as a catalyst, decreases as the mol. wt. of the alcohol increases, except with *iso*propyl alcohol, when the quantity of acetal formed in a given time is considerably less than with *iso*butyl alcohol.

The behaviour of 2-nitro-4 : 5-dimethoxybenzaldehyde, 3 : 6-dichloro-2-nitrobenzaldehyde, and 2 : 4 : 6-trinitrobenzaldehyde under similar treatment has been studied. The first named undergoes the same transformations as the parent substance. The dichloro-compound when dissolved in methyl or ethyl alcohol is converted under the influence of light into the corresponding acetal and 2 : 2′-azoxybenzoic acid derivatives, but esters of a dichloronitrosobenzoic acid are not formed, possibly because the intramolecular reaction

$$\begin{matrix}=CCl \\ -C(NO_2)\end{matrix}\!\!>C\cdot CH(OR)_2 \longrightarrow \begin{matrix}=CCl \\ -C(NO)\end{matrix}\!\!>C\cdot C(OR)_2\cdot OH$$

is prevented by steric hindrance; a solution of the aldehyde in benzene when acted on by sunlight yields 3 : 6-dichloro-2-nitrosobenzoic acid.

The formation of an ester of *o*-nitrosobenzoic acid by the decomposition of an *o*-nitrobenzaldehydeacetal undoubtedly takes place through the intermediate formation of the compound

$$NO\cdot C_6H_4\cdot C(OR)_2\cdot OH,$$

since under similar conditions *o*-nitrobenzaldehyde passes into *o*-nitrosobenzoic acid; consequently, it is extremely probable that the esterification of an acid proceeds through the mono-alkylated ortho-acid: $-CO_2H \xrightarrow{R\cdot OH} [-C(OH)_2\cdot OR] \longrightarrow -CO_2R + H_2O$, a suggestion first advanced by Henry.

The following acetals were prepared by the action of hydrogen chloride on a mixture of the aldehyde and alcohol; they were also obtained by exposing solutions of aldehyde in the necessary alcohol to the action of sunlight for a short time. o-*Nitrobenzaldehydediethylacetal*, $NO_2\cdot C_6H_4\cdot CH(OEt)_2$, is an aromatic, slightly yellow oil, b. p. 147·8—148·3°/11 mm., 154·8—155·3°/15 mm.; the corresponding *dipropylacetal*, $C_{13}H_{19}O_4N$, has b. p. 168°/10 mm.; the *di*iso*propylacetal* has b. p. 150°/12 mm.; the *di*iso*butylacetal* has b. p. 179°/11 mm.; 2-*nitro*-4 : 5-*dimethoxybenzaldehydedimethylacetal*,

$$C_{11}H_{15}O_6N,$$

crystallises in colourless, flat, glistening prisms, m. p. 54·5—55·5°.

Attempts to prepare the dimethylacetal of 2 : 4 : 6-trinitrobenzaldehyde were unsuccessful.

The following esters were prepared by acting on the requisite acetal with sunlight during a few hours; in the molten state they are green. *Propyl* o-*nitrosobenzoate*, $C_{10}H_{11}O_3N$, colourless, glistening prisms, m. p. 95°; iso*propyl* o-*nitrosobenzoate*, stout, white prisms, m. p. 117—118°; iso*butyl* o-*nitrosobenzoate*, $C_{11}H_{13}O_3N$, colourless,

compact needles, m. p. 99—99·5°; *methyl* 2-*nitroso*-4 : 5-*dimethoxybenzoate*, $C_{10}H_{11}O_5N$, faintly green, granular crystals, sinters at 125°, m. p. 126·5—127·5°.

3 : 6 : 3′ : 6′-*Tetrachloro*-2 : 2′-*azoxybenzoic acid*, $C_{14}H_6O_5N_2Cl_4$, is a pale yellow, crystalline powder, m. p. about 281—282° (decomp.), when heated in a bath from 265°. 3 : 6-*Dichloro*-2-*nitrosobenzoic acid* forms small, faintly yellow crystals. 2-*Nitro*-4 : 5-*dimethoxybenzaldoxime*, $C_9H_{10}O_5N_2$, crystallises in glistening, yellow needles, m. p. 178°, when heated in a bath from 168°. W. H. G.

Metallic Calcium and Absolute Alcohol as Reducing Agents. Charles Marschalk (*Ber.*, 1910, **43**, 641—642).—Attempts have been made to reduce coumarone and benzophenone with metallic calcium and absolute alcohol. Coumarone is not affected, but benzophenone is reduced to benzhydrol. Sodium and alcohol, on the other hand, reduce coumarone to coumaran, and benzophenone to diphenylmethane (Klages and Allendorf, Abstr., 1898, i, 433). J. J. S.

Condensation of Cuminaldehyde with Methyl Propyl Ketone. Theodor St. Warunis and P. Lekos (*Ber.*, 1910, **43**, 654—660. Compare Warunis, *Inaug. Diss.*, 1903).—Cuminaldehyde condenses with methyl propyl ketone, yielding two isomeric cuminylidenemethyl propyl ketones. These when reduced with sodium amalgam in acid solution yield isomeric cuminylmethyl propyl ketones. When treated with sodium hypochlorite according to Stoermer and Wehln's method (Abstr., 1903, i, 46), the unsaturated ketones yield cuminaldehyde.

a-Cuminylidenemethyl propyl ketone, $C_6H_4Pr^\beta \cdot CH{:}CH \cdot COPr^\alpha$, obtained by shaking the aldehyde and ketone with 10% sodium hydroxide solution, is a pale yellow liquid with b. p. 176—180°/14 mm. The *dibromide*, $C_{15}H_{20}OBr_2$, crystallises in plates, m. p. 124—125°. The *semicarbazone*, $C_{16}H_{23}ON_3$, has m. p. 163°. The *oxime*, $C_{15}H_{21}ON$, m. p. 122—123°, and the *phenylhydrazone*,

$$C_6H_4Pr^\beta \cdot CH{:}CH \cdot CPr^\alpha{:}N \cdot NHPh,$$

m. p. 111°. *a-Cuminylmethyl propyl ketone*,

$$C_6H_4Pr^\beta \cdot CH_2 \cdot CH_2 \cdot COPr^\alpha,$$

is a colourless oil, with b. p. 155—160°/12 mm., and yields a *semicarbazone*, $C_{16}H_{25}ON_3$, m. p. 126°.

γ-Cuminylidenepropyl methyl ketone, $C_6H_4Pr^\beta \cdot CH{:}CEt \cdot COMe$, obtained by saturating a mixture of the aldehyde and ketone with hydrogen chloride, is a pale yellow oil, with b. p. 174—175°/15 mm. or 167°/12 mm. The *dibromide* is oily; the *semicarbazone*, $C_{16}H_{23}ON_3$, crystallises in needles, m. p. 198°, and the *oxime*, $C_{15}H_{21}ON$, in large crystals, m. p. 107°.

γ-Cuminylpropyl methyl ketone, $C_6H_4Pr^\beta \cdot CH_2 \cdot CHEt \cdot COMe$, is a colourless liquid, b. p. 159—161°/14 mm.; its *semicarbazone*,

$$C_{16}H_{25}ON_3,$$

crystallises in plates, m. p. 135°.

The *semicarbazone* of cuminaldehyde, $C_6H_4Pr^\beta \cdot CH{:}N \cdot NH \cdot CO \cdot NH_2$, has m. p. 211°. J. J. S.

Compounds of Quinones with Esters of Amino-acids. EMIL FISCHER and HANS SCHRADER (*Ber.*, 1910, **43**, 525—529).—By the addition of an alcoholic solution of benzoquinone to a cold alcoholic solution of ethyl glycine, quinol is formed, and also a red substance, $C_{14}H_{18}O_6N_2$, which from analogy to dianilinoquinone receives the constitution $C_6H_2O_2(NH\cdot CH_2\cdot CO_2Et)_2$, and the name *diethyl diglycinoquinone.* It separates from chloroform in red, quadratic plates, has m. p. 215° (corr.), develops a fine bluish-violet colour in cold alcoholic potassium hydroxide, and by treatment with bromine in chloroform yields *ethyl glycine hydrobromide*, m. p. 175—176° (decomp., corr.).

Diethyl dialaninoquinone, $C_6H_2O_2(NH\cdot CHMe\cdot CO_2Et)_2$, m. p. 140° (corr.), crystallising in red prisms, and *diethyl diglycinotoluquinone*, $C_6HMeO_2(NH\cdot CH_2\cdot CO_2Et)_2$, m. p. 162° (corr.), are similar substances obtained in a similar manner, the solvent in the former case being ether. C. S.

Oxidation of β-Naphthaquinone. C. H. ROBINSON (*J. Amer. Chem. Soc.*, 1910, **32**, 117—119).—It has been found by Daly (Abstr., 1907, i, 407) that in the oxidation of β-naphthaquinone by an alkaline solution of potassium permanganate, the reaction ceases before the amount of permanganate has been reduced which is theoretically required to oxidise the naphthaquinone to phthalonic acid, and he has suggested that the acid $C_6H_4(CO\cdot CO_2H)_2$ may possibly be formed in the solution. Experiments have now been made which indicate that β-naphthaquinone is oxidised directly to phthalonic acid in alkaline solution without the formation of any intermediate compounds. E. G.

The Anthraquinone Series. FRITZ ULLMANN (*Ber.*, 1910, **43**, 536—539).—In this preliminary paper the author summarises briefly the results of previous work on the mobility of halogen atoms in anthraquinone derivatives. His intention is to study anthraquinone derivatives in connexion with the problem of colour and constitution, and also to examine the affinity of their leuco-compounds for the fibre. C. S.

Preparation of Chloro- and Bromo-anthraquinonesulphonic Acids. BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 216071).—The direct halogenation of anthraquinonesulphonic acids in aqueous solution does not proceed smoothly, owing to the frequent replacement of sulphonic groups by hydroxyl. It is found that if concentrated sulphuric acid, or that containing anhydride, is employed as solvent, and the required halogen introduced either in the presence or absence of a carrier, the reaction proceeds normally.

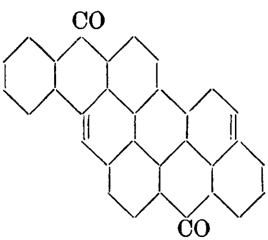
1 : 4-*Dichloroanthraquinone-β-sulphonic acid*, prepared by thus treating sodium anthraquinone-β-sulphonate with chlorine at 160° until the necessary increase of weight has been obtained, is a dark yellow powder, crystallising from 90% acetic acid in glistening, yellow scales. The position of the chlorine atoms was indicated by the formation of quinizarinsulphonic acid on replacement of halogen by hydroxyl.

Sodium bromoanthraquinonesulphonate, dark yellow, spear-shaped crystals, together with other more highly brominated acids, were prepared from sodium anthraquinone-β-sulphonate. F. M. G. M.

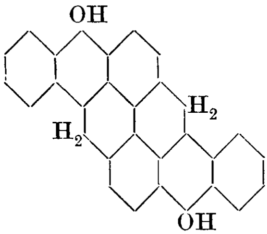
Preparation of Dianthraquinone Oxide. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216268).—*$\alpha\beta$-Dianthraquinone oxide* is prepared by condensing 1-chloroanthraquinone with 2-hydroxyanthraquinone in the presence of copper powder and fused sodium acetate in nitrobenzene solution; on cooling, the product separates in grey crystals, which are almost insoluble in all the ordinary solvents, except acetic acid. F. M. G. M.

Preparation of Dianthraquinonyl and of Dibenzanthronyl Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 215006).—Dianthraquinonyl derivatives have previously been prepared by treating the diazonium salts of aminoanthraquinones with copper in the presence of acetic anhydride (Abstr., 1907, i, 942); it is now found that the reaction will take place in dilute aqueous solutions containing copper salts, or such mixtures as cupric chloride and iron, ferric chloride and copper, potassium bromide and zinc dust, cupric chloride and hydroxylamine, or cupric chloride and sulphurous acid. The patent mentions 1 : 1′-*dianthraquinonyl* (from 1-aminoanthraquinone), 2 : 2′-*dianthraquinonyl* (from 2-aminoanthraquinone), 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (from 1-amino-2-methylanthraquinone), and *dibenzanthronyl*, prepared from aminobenzanthrone.
F. M. G. M.

Pyranthrone, A Non-nitrogenous Methine Analogue of Flavanthren, and Dimethylpyranthrone. ROLAND SCHOLL (*Ber.*, 1910, **43**, 346—356).—[With CHRISTIAN SEER.]—*Dinitro*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinoyl*, $C_{30}H_{16}O_8N_2$, a yellow, crystalline substance, is obtained by keeping a solution of dimethyldianthraquinoyl in nitric acid, D 1·52, for three to five days at the ordinary temperature. By boiling for one to two hours with sodium hydroxide and sodium hyposulphite, it is reduced to the *diamino*-compound, $C_{30}H_{20}O_4N_2$, which forms dark red, microcrystalline octahedra. The conversion of dimethyldianthraquinoyl into *pyranthrone* (annexed formula) is effected by (1) heating at 350—380° for thirty minutes, (2) heating with zinc chloride at 280° for fifteen minutes, (3) heating with alcoholic potassium hydroxide for two hours at 140—145°. In the last method a blackish-red, hydrogenised compound is produced, which is converted into pyranthrone by passing air through the reaction mixture diluted with boiling water. Pyranthrone is a brown powder, which is insoluble in low boiling solvents, but separates from nitrobenzene in reddish-brown needles with a steel-blue lustre; it is carbonised by heating, gives a blue solution in concentrated sulphuric acid, is slowly oxidised by fusion with alkalis, and by reduction with alkaline hyposulphite yields a purplish-red vat,



which regenerates pyranthrone in the presence of air, and produces on unmordanted cotton lustrous, purplish-red colours, which change in air to orange-yellow or fiery-red shades of unrivalled fastness.



[With JULIUS POTSCHIWAUSCHEG.]—The preceding vat probably contains the sodium derivative of tetrahydropyranthrone (annexed formula), because with ethereal *p*-bromobenzoyl chloride it yields *di*-p-*bromobenzoyltetrahydropyranthrone*, $C_{44}H_{24}O_4Br_2$, which forms yellow needles and does not melt below 360°. *Pyranthrene*, $C_{30}H_{18}$, is obtained by heating pyranthrone, red phosphorus, and hydriodic acid, D 1·7, for seven hours at 165—175°. It has m. p. above 360°, crystallises in brown needles or yellowish-green prisms, develops a violet-blue coloration in sulphuric acid, and forms a fluorescent solution in xylene and a non-fluorescent solution in nitrobenzene.

4-*Nitro*-1 : 3-*dimethylanthraquinone*, m. p. 234°, is obtained by boiling dimethylanthraquinone with nitric acid, D 1·37, for ten hours; it is reduced by sodium hydroxide and sodium hyposulphite to the *amino*-compound, m. p. 235—236°. 2 : 4-*Dinitro*-1 : 3-*dimethylanthraquinone*, m. p. 283—285°, is obtained by agitating dimethylanthraquinone with nitric acid, D 1·52, for ten hours at the ordinary temperature; the *diamino*-compound has m. p. 230° (decomp.). 4-*Iodo*-1 : 3-*dimethylanthraquinone*, $C_{16}H_{11}O_2I$, m. p. 118—119°, obtained from diazotised 4-amino-1 : 3-dimethylanthraquinone and potassium iodide, is converted by Ullmann's copper process at 210—250° into 2 : 4 : 2′ : 4′ *tetramethyl*-1 : 1′-*dianthraquinoyl*, $C_6H_4{<}^{CO}_{CO}{>}C_6HMe_2{\cdot}C_6HMe_2{<}^{CO}_{CO}{>}C_6H_4$, m. p. 296—298°, which by treatment with alcoholic potassium hydroxide at 135°, and subsequent oxidation of the product by air, yields 4 : 4′-*dimethylpyranthrone*, $C_{32}H_{18}O_2$. The latter separates from nitrobenzene in orange-red needles, and yields with alkaline hyposulphite a purplish-red vat, which develops on unmordanted cotton purplish-red shades changing to a fine golden-yellow in air. 4 : 4′-*Dimethylpyranthrene*, $C_{32}H_{22}$, crystallises in brown needles, and forms a fluorescent solution in *m*-xylene. C. S.

Monoterpenes, Limonenes, and Carvones. ERNST DEUSSEN and ALFRED HAHN (*Ber.*, 1910, 43, 519—524).—The new *d*-β-carvoxime (Abstr., 1909, i, 502) can be obtained from either *d*-α- or β-limonenenitrosochloride by elimination of hydrogen chloride. In a similar way, *l*-limonenenitrosochloride yields, in addition to *d*-carvoxime, an oil, which forms a *benzoyl* derivative, m. p. 76—77°, $[\alpha]_D$ − 73·58° in benzene, from which *l*-β-*carvoxime*, m. p. 56—57°, is obtained by hydrolysis by alcoholic potassium hydroxide.

d-Limonene-α-nitrolanilide and also *d*-limonene-β-nitrolanilide, when heated at 140°/12 mm., yield aniline and *l*-α-carvoxime. *l*-α-Carvoxime is converted into *i*-carvoxime by prolonged heating in alcohol or petroleum, and *l*-hydrochlorocarvoxime is also rendered inactive by

heating its methyl-alcoholic solution; the benzoyl and the phthalyl esters of *l*-α-carvoxime, however, remain unaltered under these conditions. *l*- and *d*-α-Benzoylcarvoximes yield by bromination *tetrabromo*-compounds, each having m. p. 135—136°; that derived from *l*-α-benzoylcarvoxime has $[\alpha]_D$ +25·97°, and that from the *d*-isomeride, −[25·51°], in benzene. C. S.

Ethereal Oils Free from Terpenes and Sesquiterpenes. ERICH BÖCKER (*J. pr. Chem.*, 1910, [ii], **81**, 266—281).—Frequently the odour of a natural ethereal oil is prejudicially affected, and its solubility in alcohol largely diminished, by the presence of terpenes and sesquiterpenes. A table is given comparing the specific gravity, rotation, solubility in alcohol of different strengths, saponification, ester, acid and acetylation numbers, aldehyde and phenol content, and the solidifying point of sixty-three natural ethereal oils with those of the oils left after the removal of the hydrocarbons by processes which are trade secrets. C. S.

Occurrence of Camphene in Rosin Spirit. CARLO GRIMALDI (*Chem. Zeit.*, 1910, **34**, 220).—In an earlier communication (Abstr., 1909, i, 943) the author recorded the occurrence of camphene in "spirits" prepared from American and Austrian colophony, but only in small quantities. He has now succeeded in isolating it in the pure state. E. J. R.

Characters, Distinction, and Detection in Plants of Arbutin and Methylarbutin. ÉMILE BOURQUELOT and MLLE. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1910, [vii], **1**, 62—66, 104—109).—The arbutin of commerce is now known to be a mixture of true arbutin with methylarbutin (compare Bourquelot and Hérissey, Abstr., 1908, i, 356), and in the present paper the constants and reactions of the two substances are detailed with a view to facilitating their identification in plants. Arbutin is hydrolysed by emulsin, yielding quinol and dextrose, and the cupric-reducing power of the solution resulting from the action of emulsin on a solution of the glucoside is due to both these substances. Owing to the presence in emulsin of a small amount of an oxydase, the quinol formed by the hydrolysis of arbutin in this way becomes slightly oxidised, and the solution assumes a yellowish-brown colour. This oxidation does not seriously affect the cupric-reducing power of the product so long as the action is not allowed to go on for more than eight days. Arbutin gives a blue coloration with ferric chloride solution, and a sapphire-blue colour with Jungmann's reagent.

Methylarbutin on hydrolysis by emulsin furnishes quinol methyl ether and dextrose, and the cupric-reducing power of the hydrolysed product and its rotation are due to the latter only. On hydrolysis with emulsin, a solution of methylarbutin does not darken in colour even if an oxydase is added. Further, it is hydrolysed much more rapidly than arbutin (compare Abstr., 1908, ii, 995; 1909, i, 862), and gives no coloration with either ferric chloride solution or Jungmann's reagent, although quinol methyl ether gives, like arbutin, a blue colour with each of these reagents.

For the detection of either of these glucosides in presence of the other, determination of the rotation before and after hydrolysis with emulsin is recommended, the colour reactions mentioned being used for confirmatory evidence. T. A. H.

Glucosidic Acids of Convolvulin and the Composition of Crude *iso*Rhodeose. EMIL VOTOČEK (*Ber.*, 1910, **43**, 476—482).—Convolvulin is resolved by hydrolysis with alkali into α-methylbutyric acid and two glucosidic acids, the crystalline convolvulinic acid and amorphous purgic acid. Convolvulinic acid, when hydrolysed with acids, forms convolvulinolic acid, dextrose, rhodeose, and a sugar which gives rise to mucic acid when its hydrogen cyanide additive product is oxidised; this is now proved to be rhamnose. Purgic acid is converted by acid hydrolysis into decenoic acid, hydroxylauric acid, and syrupy *iso*rhodeose; the last contains only methylpentoses, and has $[\alpha]_D + 25°$; it forms no mucic acid when the hydrogen cyanide additive product is oxidised. The *phenylosazone* has m. p. 183—184°, the p-*bromophenylosazone* has m. p. 217°, whilst *rhodeose*-p-*bromophenyl hydrazone* has m. p. 202—204°. Crystalline hydrazones could not be obtained. E. F. A.

Aloin. OTTO A. OESTERLE and G. RIAT (*Schweiz. Woch. Chem. Pharm.*, 1909, 717—721. Compare Oesterle, Abstr., 1899, i, 538; 1900, i, 304; Tschirch and Pedersen, Abstr., 1898, i, 599; Jowett and Potter, Trans., 1905, **87**, 878; Robinson and Simonsen, *ibid.*, 1909, **95**, 1085).—Aloe-emoidin and a sugar are formed when aloin is boiled for some eighty hours with sulphuric acid and 95% alcohol, or for twenty-four to thirty-six hours with alcohol and hydrochloric acid. The sugar gave an osazone, m. p. 208—209°.

The oxidation of aloin with sodium peroxide (Léger, Abstr., 1902, i, 549) has been studied. The best yields are obtained when 30 grams of aloin are warmed with 500 c.c. of water at 70—80°. Thirty grams of the peroxide are added gradually and with constant stirring. The addition of hydrochloric acid precipitates crude aloe-emoidin (compare Jowett and Potter). J. J. S.

Tetrahydrothiophen and *cyclo*Pentamethylene Sulphide. JULIUS VON BRAUN and A. TRÜMPLER (*Ber.*, 1910, **43**, 545—551).—Whilst substances containing four-, five-, six-, seven-, sixteen-, and eighteen-membered rings of carbon and at least two atoms of sulphur are formed easily and sometimes quantitatively from acyclic generators, the production of heterocyclic systems containing only one atom of sulphur is accompanied by anomalies, the comparatively easy formation of thiophen being in strong contrast to the difficulty of obtaining methylpenthiophen (Krekeler, Abstr., 1887, 239). The authors have prepared compounds of the type $(CH_2)_x{>}S$, and encounter similar anomalies. *Tetrahydrothiophen*, $\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}{>}S$, b. p. 119°, is obtained in almost quantitative yield when an alcoholic solution of $\alpha\delta$-di-iodobutane is added to a concentrated aqueous

solution of potassium sulphide, whilst under similar conditions the yield of *pentamethylene sulphide* [*pentahydropenthiophen*],

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>S,$$

b. p. 141°, from αε-di-iodopentane is less than 30%. Tetrahydrothiophen and pentamethylene sulphide, which form *methiodides* volatilising at 185—190° and 192° respectively, are very reactive substances, but their thorough examination has been postponed for the present on account of their insufferable odour. C. S.

Action of Cyanogen Bromide on Brucine and Strychnine. GUSTAV MOSSLER (*Monatsh.*, 1910, 31, 1—22).—Since brucine and strychnine probably contain a tetrahydroquinoline or a dihydroindole skeleton in which the nitrogen atom is linked to a nuclear carbonyl group, the author has applied to the two alkaloids Braun's methods of rupturing heterocyclic nitrogenous systems by means of phosphorus pentachloride (Abstr., 1904, i, 918) or cyanogen bromide (Abstr., 1900, i, 430). The attack of the former reagent does not lead to definite results, but by the action of cyanogen bromide in chloroform, additive compounds are formed which cannot be isolated in a pure state. The compound obtained from strychnine is decomposed by water, yielding ammonia and the hydrobromide of the alkaloid. The additive compound of cyanogen bromide and brucine is further attacked by the reagent in two directions, according to the experimental conditions. When cyanogen bromide is added slowly to a cold solution of brucine in chloroform, crystals are obtained of a *substance*,

$$C_{47}H_{52}O_8N_5Br,CHCl_3,3H_2O,$$

which by heating at 110° and crystallisation from 70% alcohol yields crystals of the composition $C_{47}H_{52}O_8N_5Br,2H_2O$; both have m. p. 203—205° (decomp.). The substance, which does not possess basic properties and retains its halogen in the presence of cold alkali, is regarded as a quaternary ammonium bromide produced by the rupture of one brucine molecule by the cyanogen bromide and the combination of the resulting brominated cyanamide with a second molecule of brucine.

When a solution of brucine in chloroform is added to an excess of cyanogen bromide in the same solvent, and the mixture is treated with 90% alcohol, a precipitate is obtained which by solution in water and reprecipitation by alcohol yields needles of a *hydrobromide*,

$$C_{23}H_{26}O_4N_2,HBr,4H_2O,$$

containing two methoxyl groups and decomposing at 250°. The free base, allo*brucine*, $C_{23}H_{26}O_4N_2,5H_2O$, is isomeric with brucine, into which it is converted by crystallisation from boiling water, but differs from it in containing water of crystallisation, in its rotation, $[\alpha]_D^{18} - 112\cdot6°$, in chloroform, m. p., and derivatives. The hydrated base melts at 69·5°, resolidifies at 75—80°, softens at 120—130°, and fuses again at about 182° (decomp.). The anhydrous base melts at 126—128° to a transparent, indistinctly liquid substance, becomes opaque, and then melts at about 182° (decomp.) *allo*Brucine, which is a monoacidic base, exhibits all the colour reactions of brucine. The *hydrochloride*, $C_{23}H_{26}O_4N_2,HCl,4H_4O$, crystallises in leaflets which effloresce

in air; the *methiodide*, $C_{23}H_{26}O_4N_2,MeI,1\frac{1}{2}H_2O$, has m. p. 265° (decomp.). When *allo*brucine is warmed with hydrogen peroxide, a *peroxide*, $C_{23}H_{26}O_6N_2$, is obtained, which contains $5H_2O$ when dried in air and H_2O when dried in a vacuum, and at 110° is converted into the *oxide*, $C_{23}H_{26}O_5N_2,H_2O$, which is also produced by heating an aqueous solution of the peroxide with platinum-black. The two hydrated peroxides and the oxide all have m. p. 182° (decomp.); by very rapid heating, the air-dried peroxide decomposes at 115—120° and the monohydrate at 150—152°, both resolidifying and then melting again at 182°. An aqueous solution of the peroxide is neutral and optically inactive, liberates iodine from potassium iodide, bleaches litmus, and exhibits the reactions of hydrogen peroxide when treated with potassium dichromate and sulphuric acid.

allo*Brucic acid*, $C_{23}H_{28}O_5N_2,7H_2O$, obtained by the action of sodium ethoxide on *allo*brucine, crystallises in yellow needles, has m. p. 165—166° (decomp.) when anhydrous, forms a nitrosoamine, the *hydrochloride* of which, $C_{23}H_{28}O_6N_3Cl$, carbonises at 210°, and is stable in boiling water, but is converted by cold acids into the corresponding brucine salts. C. S.

Hofmann's Iodomethylation of Cinchotoxine. I. Constitution of Freund and Rosenstein's Dimethylcinchonine. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 240—254).—Assuming the accuracy of the formula

$$C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH{<}{\begin{matrix}CH(CH\!:\!CH_2)\\ CH_2\cdot CH_2\cdot NH\end{matrix}}{>}CH_2$$

for α-cinchonicine (cinchotoxine) (compare Abstr., 1909, i, 409), the dimethylcinchonine prepared by Freund and Rosenstein (Abstr., 1894, i, 151) will have one of the two formulæ:

$$C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH(CH_2\cdot CH_2\cdot NMe_2)\cdot C(CH\!:\!CH_2)\!:\!CH_2 \quad (I)$$

and $C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot CH(CH\!:\!CH_2)\cdot CH(CH\!:\!CH_2)\cdot CH_2\cdot NMe_2$ (II). The author's experiments show that oxidation of dimethylcinchonine (1 mol.) by means of cold permanganate yields 1 mol. of formic acid, together with an unsaturated acid compound, which is named dimethylcinchotenine, thus: $-CH\!:\!CH_2 + 4O \longrightarrow H\cdot CO_2H + -CO_2H$.

[With ONOFRIO D'ONGHIA.]—*Dimethylcinchoninephenylhydrazone*, $C_{19}H_{20}N_2Me_2\!:\!N_2HPh$, forms yellow, mamillary crystals, m. p. 101—103°.

Tetrabromodimethylcinchonine hydrobromide,

$$C_{19}H_{16}ON_2Br_4Me_2,2HBr,$$

forms a dark yellow, deliquescent powder, m. p. 20—22°. The *picrate*, $C_{19}H_{16}ON_2Br_4Me_2,HBr,C_6H_3O_7N_3$, forms a lemon-yellow, crystalline powder, m. p. 143—145°. The *platinichloride*,

$$C_{19}H_{16}ON_2Br_4Me_2,H_2PtCl_6,$$

is obtained as a dark yellow powder, m. p. 230°, and the *aurichloride*, $C_{19}H_{16}ON_2Br_4Me_2,2HAuCl_4$, in reddish-yellow granules, m. p. 85° (decomp.).

Dimethylcinchotenine forms a reddish-brown powder with an acid reaction, and turns brown and contracts at 250°. Its *dibromo*-derivative, $C_{18}H_{16}ON_2Br_2Me_2\cdot CO_2H$, is obtained as a reddish-brown powder, which contracts at 200°, but does not melt at 250°. T. H. P.

Synthesis of Pyrrole Derivatives: Pyrroles from Ethyl Succinylosuccinate and from Azines. OSCAR PILOTY (*Ber.*, 1910, 43, 489—498).—Piloty and Quitmann (this vol., i, 133) have shown that hæmopyrrole and hæmopyrrolecarboxylic acid are trisubstituted pyrrole derivatives, and consider that the hæmatin or hæmin molecule, $C_{34}H_{34}O_4N_4FeCl$ or $C_{34}H_{32}O_4N_4FeCl$, contains each of these units repeated twice. Four such units contain 52 atoms of hydrogen, so that 20 or 18 atoms must be eliminated in the condensation.

One method of realising this is the formation of an intermediate ring from the side-chains of two molecules. Tryptophan, for example, might condense to yield derivatives of the parent substance,

$$CH{<}\begin{matrix}CH\text{–}C\cdot CH_2\cdot C\cdot NH\\ \quad\ \ \| \qquad\quad \| \\ NH\cdot C\cdot CH_2\cdot C\text{–}CH\end{matrix}{>}CH,$$

which may be termed *hydropyrrindole*. The possibility of tryptophan having some relation to the colouring matter of blood has already been emphasised by Abderhalden.

Knorr's pyrrole synthesis can be extended to the condensation of 2 mols. of aminoacetone with 1 mol. of ethyl succinylosuccinate, forming *dimethylhydropyrrindole*, $CH{<}\begin{matrix}CMe\cdot C\cdot CH_2\cdot C\text{–}NH\\ \qquad \| \qquad\quad \| \\ NH\text{–}C\cdot CH_2\cdot C\cdot CMe\end{matrix}{>}CH.$

This substance is inclined to polymerise, and forms red, green, and violet dyes when oxidised. The full investigation has been delayed by the poor yields obtained, the constitution being assumed from the method of formation.

A more promising method of obtaining pyrrole derivatives is by the action of zinc chloride at high temperatures on the azines of aliphatic ketones. Bisdiethylazinemethylene gives rise to 3 : 4-*dimethyl*-2 : 5-*diethylpyrrole*, $NH{<}\begin{matrix}CEt{:}CMe\\ \quad\ \ | \\ CEt{:}CMe\end{matrix}.$

The condensation of aminoacetone hydrochloride with ethyl succinylosuccinate takes place in sodium hydroxide solution. *Dimethylhydropyrrindole*, purified by sublimation in a vacuum, forms colourless, lustrous, nacreous plates, which sinter at 260°, m. p. 271°. It gives a cherry or violet-red coloration with ferric chloride.

By the action of solid potassium hydroxide on aminobutanone hydrochloride, tetramethylpyrazine is formed, m. p. 86—87°, together with a pyrrole derivative, which was not obtained crystalline and decomposed into tetramethylpyrazine when distilled.

3 : 4-*Dimethyl*-2 : 5-*diethylpyrrole* is obtained as a faintly yellow-coloured oil, b. p. 133—135°/55 mm. The ethereal solution becomes dark brown on the addition of picric acid without yielding a picrate. It forms an amorphous *potassium* salt. The *acetate* is a light yellow oil, b. p. 180—184°/88 mm. E. F. A.

Anthranil. XVII. Heller's Recent Experiments in Connexion with Anthranil. EUGEN BAMBERGER (*J. pr. Chem.*, 1910, [ii], 81, 254—265).—To disprove Heller's statement that aniline, not anthranil, is the product obtained by heating anthroxanic acid with water at 150° (Abstr., 1909, i, 832), the author has performed nine experiments in which anthroxanic acid (1 gram) is heated with 40—60 grams of water

at temperatures between 145° and 156° and for periods varying between three and four hours, and in every case anthranil can be detected by its odour, and frequently, also, by the formation of the mercurichloride.

In reply to Heller's contention (*loc. cit.*) that 23% hydrochloric acid and sodium nitrite act as a chlorine generator, the author shows that the nitrite produces less than 0·5% of chlorine from hydrochloric acid of this dilution. C. S.

[Preparation of Isatin Derivatives.] KALLE & Co. (D.R.-P. 215785. Compare Abstr., 1907, i, 1073).—Alkyloxyisatins having the general formula $OR\cdot C_6H_4<\substack{CO\\NH}>CO$, R = alkyl, can be readily obtained by known methods for the preparation of isatins.

7-*Methoxyisatin*, $OMe\cdot C_6H_3<\substack{CO\\NH}>CO$, bluish-red needles, m. p. 240—242°, is formed (1) by the oxidation of dimethoxyindigotin, (2) from the cyanohydrin of di-*o*-methoxycarboxydiphenylimide, (3) from di-*o*-anisyloxalimide chloride (Abstr., 1908, i, 695). 5-*Methoxyisatin*, prepared from *o*-nitro-*m*-methoxybenzaldehyde, forms brownish-red needles, m. p. 200—202°.

The condensation products from these compounds with 3-oxy-(1)-thionaphthen and with 6-ethoxy-3-oxythionaphthen-2-carboxylic acid form valuable vat dyes. F. M. G. M.

Indigoid Dyes. VI. A. FELIX and PAUL FRIEDLÄNDER (*Monatsh.*, 1910, 31, 55—79. Compare Abstr., 1908, 673, 674; 1909, 415, 417; this vol., i, 176).—Indigoid dyes are obtained by the action of α-isatin chloride or anilide on keto- and diketo-hydrindene, various coumaranones, and dihydroxy*iso*quinolines. The dyes are very similar to indigotin, but give redder shades, and are more sensitive towards alkalis; they are sparingly soluble, crystalline substances, which can be sublimed and be reduced in alkaline solution to easily oxidisable leuco-compounds. The following dyes of these types have been prepared: 2-*Indane-2-indole-indigo* [2(2′)-*indoxyl*-3-*indanone*],

$$C_6H_4<\substack{CO\\CH_2}>C{:}C<\substack{CO\\NH}>C_6H_4,$$

prepared by heating equal molecular quantities of hydrindone and isatin chloride in benzene, crystallises in red needles, and is reduced by alkaline hyposulphite to a yellow vat, from which cotton is dyed bluish-red. 2(2′)-*Indoxyl*-1 : 3-*indandione*,

$$C_6H_4<\substack{CO\\CO}>C{:}C<\substack{CO\\NH}>C_6H_4,$$

obtained in a similar manner from diketohydrindene, forms brownish-violet needles, and is decomposed by warming with 5% sodium hydroxide, yielding anthranilic acid and 3-*hydroxy*-1-*indenone*-2-*aldehyde*, $C_6H_4<\substack{C(OH)\\CO}>C\cdot CHO$, m. p. 139·5°, which separates from hot water in white, and from organic solvents in red needles, reacts with hydrazine and phenylhydrazine, develops a cherry-red colour with ferric chloride, and forms yellow alkali salts which are not decomposed by acetic acid. 5 : 6-*Dimethoxy*-1(2′)-*indoxylcoumaranone*

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}C<\substack{CO\\NH}>C_6H_4$, obtained from *a*-isatinanilide and dimethoxycoumaranone in naphtha, forms copper-red crystals, which yield a reddish-violet vapour almost without decomposition. Hydroxymethoxycoumaranone and isatinanilide under similar conditions yield an analogous indigoid dye, $C_{17}H_{11}O_5N$. Both of these dyes in alcoholic or acetic acid solution react with aldehydes in the presence of sodium carbonate or hydrochloric acid to form oxygen isologues of the indogenides, of which the following are described:

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}CHPh$, from benzaldehyde, yellow prisms, m. p. 148—149°.

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}CH\cdot C_6H_4\cdot OH$, from salicylaldehyde, orange-yellow needles, m. p. above 240°.

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}CH\cdot C_6H_4\cdot OH$, from *m*-hydroxybenzaldehyde, yellow needles, m. p. 202·5—203°.

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}CH\cdot C_6H_4\cdot OH$, from *p*-hydroxybenzaldehyde, citron-yellow crystals.

$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}CH\cdot C_6H_2(OH)_2$, from protocatechualdehyde, orange-yellow needles, m. p. 217°.

The *dimethoxycoumaranone*, m. p. 122·5—123°, required in the preceding preparation is obtained by adding an excess of methyl sulphate to a warm solution of ω-chlorotrihydroxyacetophenone (obtained from pyrogallol and chloroacetic acid) in aqueous sodium carbonate. In faintly alkaline solution, and with a deficit of methyl sulphate, the monomethylated *derivative*, m. p. 197°, is also produced. A dilute alcoholic solution of equal molecular quantities of dimethoxycoumaranone and *β*-naphthaquinone-4-sulphonic acid, by treatment with aqueous sodium carbonate, yields the sodium salt of 5′ : 6′-*dimethoxycoumaranonyl*-1-*hydroxy*-4-*oxynaphthalene*,

$$C_6H_2(OMe)_2<\substack{CO\\O}>C{:}C<\substack{\text{—}C_6H_4\text{—}\\CH{:}C(OH)}>CO,$$

which crystallises in orange-brown needles. 3(2′)-*Indoxyl*-3-iso*quinoline*-1 : 4-*dione*, $C_6H_4<\substack{CO\cdot C\\CO\cdot NH}>C<\substack{CO\\NH}>C_6H_4$, prepared from *a*-isatin chloride or anilide and dihydroxy*iso*quinoline, forms dark blue needles, and is reduced by alkaline hyposulphite to an orange-red vat, from which the dye is regenerated in the air.

Indigoid dyes have also been produced by the action of isatin chloride or anilide on rhodanic acid, methylpyrazolone, phenylmethylpyrazolone, and barbituric acid. The increased aliphatic character of these dyes is accompanied by increased sensitiveness towards acids and, especially, alkalis. 5-*Keto*-4(2′)-*indoxyl*-1-*phenyl*-3-*methylpyrazole*, $\substack{NPh\cdot CO\\N{=}CMe}>C{:}C<\substack{CO\\NH}>C_6H_4$, obtained from phenylmethylpyrazolone and isatin-*a*-anilide in boiling xylene, separates

from nitrobenzene in almost black plates, gives a light yellow vat with alkaline hyposulphite, and is decomposed by boiling 10% sodium hydroxide, yielding anthranilic acid and 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*aldehyde*, $COH\cdot C\begin{matrix} \diagup C(OH)\cdot NPh \\ \diagdown CMe = N \end{matrix}$, m. p. 173—174°. This aldehyde is amphoteric, the acid character predominating; it forms a fairly stable *silver* salt, a *phenylhydrazone*, m. p. 159°, an *aldazine*, m. p. 290°, and the *azomethine* derivative, $\begin{matrix} NPh\cdot C(OH) \\ N \!=\!=\! CMe \end{matrix}\!\!>\!C\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, m. p. 240°, with anthranilic acid in the presence of dilute acids. 4(2′)-*Indoxyl*-3-*methyl*-4-*pyrazole*, $\begin{matrix} NH\cdot CO \\ N{:}CMe \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} CO \\ NH \end{matrix}\!\!>\!C_6H_4$, obtained from equal molecular quantities of 3-methylpyrazolone and isatinanilide in nitrobenzene at 150°, separates from alcohol or dilute acetic acid in dark violet needles; it possesses pronounced basic properties, and is easily decomposed by alkali hydroxides. 4-*Keto*-2-*thio*-5(2′)-*indoxylthiazole*, $\begin{matrix} NH\cdot CO \\ CS-S \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} CO- \\ NH \end{matrix}\!\!>\!C_6H_4$ or $\begin{matrix} N-CO \\ C(SH)\cdot S \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} CO- \\ NH \end{matrix}\!\!>\!C_6H_4$, obtained by heating rhodanic acid and α-isatinanilide in acetic anhydride, forms almost black needles. 4-*Keto*-2-*thio*-5(2′)-*thionaphthenylthiazole*, $\begin{matrix} NH\cdot CO \\ CS-S \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} CO \\ S \end{matrix}\!\!>\!C_6H_4$, obtained from thioisatinanilide and rhodanic acid in a similar manner, forms reddish-brown needles. 5(2′)-*Indoxylpyrimidine*-2 : 4 : 6-*trione*,

$$CO\!<\!\begin{matrix} NH\cdot CO \\ NH\cdot CO \end{matrix}\!\!>\!C{:}C\!<\!\begin{matrix} CO- \\ NH \end{matrix}\!\!>\!C_6H_4,$$

prepared from barbituric acid and α-isatinanilide in acetic anhydride, forms orange-red needles.

The absorption spectra of those indigoid dyes which differ from indigotin by containing, in the place of one of the NH groups, the atoms or groups: S, CH:CH, CO·NH, CH_2, or CO, are plotted, and the influence of these replacements on the colour are briefly discussed.

C. S.

Coloured Salts of Schiff's Bases. III. Salts of Bases Formed by Condensing *m*-Aminodimethylaniline and *m*-Aminodiethylaniline with Aromatic Aldehydes. FORRIS J. MOORE (*J. Amer. Chem. Soc.*, 1910, **32**, 382—388).—It has been shown in earlier papers (Moore, Abstr., 1908, i, 368; Moore and Woodbridge, Abstr., 1908, i, 686) that benzylidene compounds of the type $R\cdot CH{:}N\cdot C_6H_4\cdot NR'R''$ unite with hydrogen chloride in two proportions, forming dark red hydrochlorides and yellow dihydrochlorides.

The present work was undertaken with the object of determining whether the difference in the colour of these salts is due to the dark-coloured salts having a quinonoid constitution. In order to test this, it was decided to prepare analogous compounds of such a structure that they could not readily assume the quinonoid form, and to study their salts. It seems probable that the bases previously used in this work would readily form quinonoid salts, since, in all cases, the two

nitrogen atoms were in the para-position to each other. This behaviour, however, would not be expected from the analogous meta-compounds.

as-Dimethyl-*m*-phenylenediamine and *as*-diethyl-*m*-phenylenediamine condense readily with benzaldehyde, anisaldehyde, cinnamaldehyde, and piperonaldehyde to form *compounds*, which on treatment with hydrogen chloride invariably yield light-coloured *salts*. This behaviour seems at first sight to indicate that the dark-coloured salts of the corresponding *p*-compounds have a quinonoid structure, but this inference is weakened by the fact that the *m*-bases are polymerides, and can only be obtained in an amorphous condition.

m-Nitrodiethylaniline and *as*-diethyl-*m*-phenylenediamine *picrates* melt at 138° and 152° respectively. E. G.

Preparation of Benzophenoneimine Derivatives. FORRIS J. MOORE (*Ber.*, 1910, **43**, 563—565. Compare Reddelien, this vol., i, 118).—Diphenylmethylenedimethyl-*p*-phenylenediamine, m. p. 86°, is readily obtained by heating together equivalent quantities of benzophenone and *p*-aminodimethylaniline with finely-powdered barium oxide in an atmosphere of hydrogen at 180°. With other amines the condensation proceeds more readily in the absence of the barium oxide. Thus benzophenonephenylimine is readily obtained by heating benzophenone and aniline for an hour at 210°.

Benzophenoneimine hydrobromide is readily obtained by passing ammonia into a chloroform solution of diphenyldibromomethane (Friedel and Balsohn, Abstr., 1880, 558). It crystallises in colourless needles and reacts with water, yielding benzophenone. The free base can be obtained by Hantzsch's (Abstr., 1892, 338) or Thomae's (Abstr., 1905, i, 718) method.

A small amount of the hydrobromide is also formed by the action of magnesium phenyl bromide on benzobromoamide. J. J. S.

Preparation of Dianthraquinonylphenylenediamine. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 215294).—*Dianthraquinonylphenylenediamine*, $C_6H_4(NH\cdot C_6H_3{<}^{CO}_{CO}{>}C_6H_4)_2$, is prepared by condensing aminoanthraquinone with *p*-dichlorobenzene in the presence of naphthalene, sodium acetate, and cupric chloride at 200—215°. The product crystallises from nitrobenzene in black needles; the solution in concentrated sulphuric acid is greenish-yellow, from which water precipitates a violet-red powder. F. M. G. M.

Tetramethyldiaminobenzophenone and Dianilinodiphenylmethane. FRITZ STRAUS and RICHARD BORMANN (*Ber.*, 1910, **43**, 728—739).—The authors cannot state with certainty that the blue compounds obtained by the action of carbonyl chloride on tetramethyldiaminobenzophenone (Staudinger, Abstr., 1909, i, 905) and tetramethyldiaminothiobenzophenone (Baither, Abstr., 1887, 816) are identical; the bishydrochloride of the former is colourless, that of the latter yellow, becoming colourless in the presence of excess of hydrogen chloride and yellow again when kept over potassium hydroxide.

Di-p-*nitro*-o-*sulphoanilinodiphenylmethane*, $CH_2[C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3H]_2$, obtained in the form of the sodium salt by heating diaminodiphenylmethane with an aqueous solution of sodium hydrogen carbonate and sodium *p*-nitrochlorobenzene-*o*-sulphonate (3 mols.), is an orange-yellow powder. If only 2 mols. of the sulphonate are used, the chief product is the sodium salt of *amino*-p-*nitro*-o-*sulphoanilinodiphenylmethane*, $NH_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3H$, a citron-yellow powder. An aqueous solution of the sodium salt of the disulphonate is reduced by zinc dust and ammonium chloride to the corresponding *amino*-compound, $C_{25}H_{24}O_6N_4S_2$, which is converted by concentrated hydrochloric acid at 100° into the *hydrochloride*, $C_{25}H_{24}N_4,4HCl$, of di-*p*-aminophenyldiaminodiphenylmethane. The *base* itself, m. p. 131°, forms white needles; its alcoholic solution, when treated in a freezing mixture with concentrated sulphuric acid and amyl nitrite, and subsequently with copper powder, yields p : p-*dianilinodiphenylmethane*, $CH_2(C_6H_4\cdot NHPh)_2$, m. p. 114°, which is soluble in concentrated acids.

C. S.

Magnesium Alkyl Haloids and Aldazines. MAX BUSCH and MARTIN FLEISCHMANN (*Ber.*, 1910, **43**, 740—750).—Franzen and Deibel found that benzaldazine was reduced to benzaldehydebenzylhydrazone by magnesium ethyl bromide (Abstr., 1905, i, 843). The authors find that, in addition to this reaction, which may proceed to the extent of forming dibenzylhydrazine, the normal addition occurs, the course of the reaction being most conveniently followed by the use of magnesium aryl halides. Thus the product of the interaction of benzaldazine and magnesium phenyl bromide in ether, when decomposed by dilute hydrochloric acid at 0°, yields a mixture of the hydrochlorides of benzaldehydebenzylhydrazone and benzaldehydediphenylmethylhydrazone. The *hydrazone* itself, $CHPh_2\cdot NH\cdot N\colon CHPh$, decomposes at 85°, explodes very readily, and easily loses its nitrogen, yielding products from which tetraphenylethane and diphenylmethane have been isolated. To account for their formation, the authors offer the suggestion that the hydrazone changes into the azo-compound, $CHPh_2\cdot N\colon N\cdot CH_2Ph$, which then decomposes like Thiele's azomethane, yielding nitrogen, diphenylmethyl, and benzyl, from the last two of which the two hydrocarbons in question are generated. The interaction of magnesium benzyl chloride and benzaldazine, and the treatment of the product successively with ice-water, acetic acid, ammonium chloride, and excess of ammonium hydroxide, lead to the formation of *benzaldehydediphenylethylhydrazone*, $CHPh\colon N\cdot NH\cdot CHPh\cdot CH_2Ph$, m. p. 104—105° (decomp.), which forms a *hydrochloride*, m. p. 124°, and is converted by benzoyl chloride in pyridine into *β-benzoyl-a-diphenylethylhydrazine*, $NHBz\cdot NH\cdot CHPh\cdot CH_2Ph$, m. p. 144°. The chief product of the interaction of magnesium ethyl bromide and benzaldazine is benzaldehydebenzylhydrazone (Franzen and Deibel, *loc. cit.*); with an excess of the organo-magnesium bromide (4 mols.), however, the main products are those formed by the decomposition of the initially formed benzaldehydephenylpropylhydrazone, namely, benzaldehyde and

γδ-diphenylhexane. The reaction between anisaldazine and magnesium benzyl chloride leads to the formation of two *substances*, one having m. p. 84° (decomp.), the other decomposing at 99°; since both have the same properties and composition, and yield anisaldehyde by treatment with mineral acids, they are regarded as the stereoisomeric modifications of *methoxybenzaldehydemethoxydiphenylethylhydrazone*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}CH(CH_2Ph){\cdot}C_6H_4{\cdot}OMe.$$

C. S.

Opening of the Glyoxaline Ring. ADOLF WINDAUS (*Ber.*, 1910, **43**, 499—501).—Glyoxaline and its homologues, alkylated in the α- and β-positions, on treatment with benzoyl chloride and sodium hydroxide are converted into dibenzoyl derivatives of unsaturated diamines, but glyoxaline derivatives containing a free carboxyl group in the side-chain are stable towards these reagents. The stability is due to the presence of the free carboxyl group, as glyoxalylpropionanilide is very readily converted into an unsaturated diamino-acid.

Glyoxalylpropionanilide, $CH{<}\begin{matrix}NH{\cdot}CH \\ \| \\ N{-\!-}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh\end{matrix}$, formed by heating glyoxalylpropionic acid with aniline at 185°, forms short, prismatic crystals, m. p. 190—191°. The *oxalate* forms four-sided plates; the *picronolate*, long, light yellow needles; the *platinichloride* crystallises in bright orange, fork-like needles; the *silver* salt is colourless.

On heating with benzoyl chloride and potassium hydroxide, the ring is broken, and the *dibenzoyl* compound

$$COPh{\cdot}NH{\cdot}CH{:}C(NH{\cdot}COPh){\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$$

is formed, crystallising in long, lustrous needles, m. p. 197°.

E. F. A.

Action of 1-Chloro-2:4-dinitrobenzene on Pyridine Bases. FRITZ REITZENSTEIN and GEORG STAMM (*J. pr. Chem.*, 1910, [ii], **81**, 160—166).—Phenanthroline or γ-dipyridyl reacts with 1-chloro-2:4-dinitrobenzene in boiling acetone to form an unstable substance, probably by the addition of 1 mol. of chlorodinitrobenzene to each of the nitrogen atoms; these additive compounds are isolated as the *platinichlorides*, $[C_{12}H_8N_2,2C_6H_3(NO_2)_2Cl],H_2PtCl_6$, m. p. above 300°, and $[C_{10}H_8N_2,2C_6H_3(NO_2)_2Cl],H_2PtCl_6$, sintering above 270°. When aniline is also present in the solution, the additive compound is not produced, 2:4-dinitrodiphenylamine being obtained by the interaction of the aniline and the chlorodinitrobenzene.

C. S.

Quinazolines. XXIV. Oxalylanthranilic Compounds and Quinazolines Derived Therefrom. MARSTON T. BOGERT and ROSS A. GORTNER (*J. Amer. Chem. Soc.*, 1910, **32**, 119—128).—This paper gives an account of compounds derived from oxalylanthranilic acid, which was first obtained by Kretschy (Abstr., 1883, 674; 1884, 750). When methoxalyl- and ethoxalyl-anthranilic acids and oxalyldianthranilic acid (Mauthner and Suida, Abstr., 1889, 139) are heated with acetic anhydride, they are converted into acylanthranils, $\begin{matrix}C_6H_4 \\ | \\ CO{-\!-}\end{matrix}{>}N{\cdot}CO{\cdot}CO_2R$

and $\begin{matrix}C_6H_4\\ CO\end{matrix}{>}N\cdot CO\cdot CO\cdot N{<}\begin{matrix}CO\\ C_6H_4\end{matrix}$. Methoxalyl- and ethoxalyl-anthranil condense with primary amines to form the corresponding quinazolines, $C_6H_4{<}\begin{matrix}N{=}C\cdot CO_2R\\ CO{-}NR'\end{matrix}$.

Methoxalylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Me$, m. p. 176·5° (corr.), obtained together with some oxalyldianthranilic acid by heating anthranilic acid (1 mol.) with methyl oxalate (1 mol.) at 140—155°, forms colourless crystals. Ethoxalylanthranilic acid has m. p. 184° (corr.). Oxalyldianthranilic acid can be prepared by heating anthranilic acid (2 mols.) with ethyl oxalate (1 mol.), as stated by Mauthner and Suida (*loc. cit.*), or by the action of oxalyl chloride on the acid.

Methoxalylanthranil, $\begin{matrix}C_6H_4\\ CO\end{matrix}{>}N\cdot CO\cdot CO_2Me$, m. p. 177·5° (corr.), forms light brown needles, and is readily hydrolysed by water. *Ethoxalylanthranil*, m. p. 129—130° (corr.), crystallises in large, colourless plates, and is more stable than the methyl derivative, but is rapidly hydrolysed by boiling water. *Oxalyldianthranil*, m. p. about 345° (uncorr.), forms a yellow powder, and is hydrolysed slowly by boiling water and rapidly by hot concentrated hydrochloric acid.

When ethoxalylanthranil is treated with alcoholic ammonia it is converted into *ammonium* 4-*quinazolone*-2-*carboxylate*, m. p. 229° (decomp.). 4-*Quinazolone*-2-*carboxylic acid* (4-*hydroxyquinazoline*-2-*carboxylic acid*), $C_6H_4{<}\begin{matrix}N{=}C\cdot CO_2H\\ CO{-}NH\end{matrix}$, forms white, silky needles, and melts at 230° (corr.) with evolution of carbon dioxide and formation of 4-quinazolone (4-hydroxyquinazoline), m. p. 214° (corr.). By heating ethoxalylanthranil with carbamide at 140—150°, *ethyl* 4-*quinazolone*-2-*carboxylate*, m. p. 185·5° (corr.), is produced. When ethoxalylanthranil (1 mol.) is heated with an aqueous solution of methylamine (2 mols.), 3-*methyl*-4-*quinazolone*-2-*carboxymethylamide*,

$$C_6H_4{<}\begin{matrix}N{=}C\cdot CO\cdot NHMe\\ CO{-}NMe\end{matrix},$$

m. p. 160° (corr.), is produced, which forms pale rose-coloured prisms. Methoxalylanthranil reacts with aniline to form *methyl* 3-*phenyl*-4-*quinazolone*-2-*carboxylate*, $C_6H_4{<}\begin{matrix}N{=}C\cdot CO_2Me\\ CO{-}NPh\end{matrix}$, m. p. 203·5° (corr.), which crystallises in small, colourless plates. The corresponding *ethyl* ester, m. p. 160° (corr), is accompanied in its formation by *ethyl* 4-*phenylimino*-3-*phenylquinazoline*-2-*carboxylate*,

$$C_6H_4{<}\begin{matrix}N{=}C\cdot CO_2Et\\ C(NPh)\cdot NPh\end{matrix},$$

m. p. 291° (decomp.), which forms a colourless, crystalline powder. *Ethyl* 4-*β*-*naphthylimino*-3-*β*-*naphthylquinazoline*-2-*carboxylate*, m. p. 253—254° (corr.), is similarly obtained as a grey, crystalline powder. When ethoxalylanthranil (1 mol.) is heated with phenylhydrazine (1 mol.), *ethyl* 3-*anilino*-4-*quinazolone*-2 *carboxylate*,

$$C_6H_4{<}\begin{matrix}N{=}C\cdot CO_2Et\\ CO{-}N\cdot NHPh\end{matrix},$$

m. p. 142° (corr.), is produced, which forms long, lemon-yellow needles. By the action of hydrazine hydrate on ethoxalyl- or methoxalyl-anthranil, s-*bis*-3-*amino*-4-*quinazolone*-2-*carboxylic hydrazide*,

$$\left[C_6H_4<\begin{matrix}N{=}C\cdot CO\cdot NH\cdot \\ CO\cdot N\cdot NH_2\end{matrix}\right]_2,$$

m. p. 157—158° (corr.), is obtained as a yellow, amorphous solid. When this compound is boiled with concentrated hydrochloric acid, it is converted into 3-*amino*-2-*carbazino*-4-*quinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CO\cdot NH\cdot NH_2 \\ CO\cdot N\cdot NH_2\end{matrix},$$

m. p. 202·5° (corr.), which crystallises in transparent plates; its *hydrochloride* has m. p. 190—191° (corr.), and its *diacetyl* derivative, $C_6H_4<\begin{matrix}N{=}C\cdot CO\cdot NH\cdot NHAc \\ CO\cdot N\cdot NHAc\end{matrix}$, has m. p. 125° (corr.). E. G.

Indanthren and Flavanthren. XII. Products of the Action of Nitric Acid on Flavanthren. Elementary Analysis of Difficultly Combustible Substances Rich in Carbon. KARL HOLDERMANN and ROLAND SCHOLL (*Ber.*, 1910, **43**, 340—345. Compare Abstr., 1908, i, 696).—When flavanthren (Abstr., 1907, i, 540) is boiled for eight hours with a mixture of nitric acid, D 1·52, and concentrated sulphuric acid, at least three products are obtained, of which the least soluble has been examined. It is a yellow, microcrystalline powder of the composition $C_{28}H_8O_{10}N_6$, and appears to be a *dinitrodinitrosodihydroxyflavanthren*. It is unchanged by sulphurous acid, forms a black *potassium* derivative, yields *dinitrosodianilinodihydroxyflavanthren*, $C_{40}H_{20}O_6N_6$, when boiled with aniline, and is reduced by alkaline hyposulphite to the blue vat dye of *tetraaminodihydroxyflavanthren*; the latter is obtained by reduction with ammonium sulphide and ammonium hydroxide, and is a blue substance resembling indigo. It is again reduced by alkaline hyposulphite to the deep blue vat dye, which produces on unmordanted cotton bluish-black shades, turned green by hydrochloric acid, the original shade being restored by treatment with water.

The estimation of the carbon and the nitrogen in anthracene derivatives of high molecular weight, which may be several units % too low by the ordinary processes, may be accurately effected by the Dennstedt method or by modifications of the ordinary processes which are described by the author. C. S.

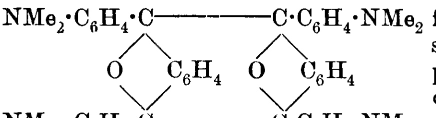
Addition Theory. ARTHUR MICHAEL (*Ber.*, 1910, **43**, 621—627). —The conclusion is drawn that the results obtained by Acree, Johnson, Brunel, Shadinger, and Nirdlinger with urazoles (Abstr., 1908, i, 919) are in complete harmony with the author's theory of addition. Acree's investigations merely show that the laws of mass action hold good in the reactions between urazole salts and alkyl halides.

The views held by Acree on the mechanism of tautomeric changes are not based on experimental facts, and are untenable. J. J. S.

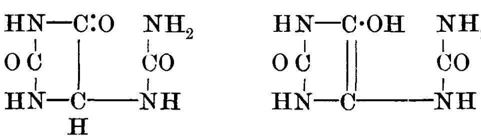
Phthaleins and Dibenzoylbenzenes. ALFRED GUYOT and ALBIN HALLER (*Ann. Chim. Phys.*, 1910, [8], **19**, 297—353).—This paper

consists mainly of a résumé of previous communications, together with further experimental details (compare Abstr., 1898, i, 670; 1900, i, 170; 1901, i, 146, 270, 350; 1903, i, 348, 748; 1904, 83, 314, 659, 660; 1905, 188, 226, 270, 516, 540; 1906, i, 761; 1907, i, 76, 565; 1908, i, 569).

The dehydration of tetramethyldiaminotriphenylmethane-*o*-carboxylic acid is best effected by heating the substance with acetic anhydride. The yield is 92%, and the product probably has the annexed constitution of a furfuran derivative. Details are given for the preparation of tetramethyldiaminodibenzoylbenzene from the product. When the substance is heated with sulphuric acid, depolymerisation occurs, and a *compound*, $C_{24}H_{24}ON_2$, is obtained. This crystallises in orange-red prisms, m. p. 140°, showing an orange-yellow phosphorescence when heated, and readily reverting to the original substance. The action of sulphuric acid leads also to the formation of a higher polymeride, occurring as a pale yellow, crystalline mass. W. O. W.



The Optical Inactivity of Allantoin. LAFAYETTE B. MENDEL and HENRY D. DAKIN (*J. Biol. Chem.*, 1910, **7**, 153—156).—Ackermann draws attention to the fact that the substances derived by putrefaction from optically active protein derivatives are themselves optically inactive. Bacteria are prone to attack the $C^*H(NH_2)\cdot CO_2H$ group, and the removal of this group abolishes molecular asymmetry. Allantoin, however, contains an asymmetric carbon atom according to the accepted formula, but no examination of its actual behaviour has yet been made. Allantoin of urinary origin was found to be inactive. An attempt to effect a resolution of the inactive substance by bacterial action failed. Several possibilities are discussed to explain the inactivity: the one most favoured is that allantoin exhibits tautomerism; thus it may be represented by the two annexed formulæ: the first is the usual one, whilst the second contains no asymmetric carbon atom. W. D. H.



(I.) (II.)

Influence of Hydroxyl Ions on Azo-coupling. II. GUSTAV HELLER [with WILHELM E. GALLEH] (*J. pr. Chem.*, 1910, [ii], **81**, 184—187. Compare Abstr., 1908, i, 300).—Solutions of benzenediazonium chloride (1 mol.), prepared in the usual way, are added to aqueous solutions of phenol (1/3 mol.) containing sodium hydroxide ($1\frac{5}{6}$ mol.), together with 20, 40, 70, or 100 grams excess of the alkali. The amount of bisbenzeneazophenol increases slowly, but continuously, that of trisbenzeneazophenol decreases very largely and rapidly, as the concentration of the alkali increases. The by-products are regarded as

O-azo-compounds, since by prolonged heating with alcohol they are converted into bis- and tris-benzeneazophenol. The conversion of the *O*-azo-compounds into real azo-compounds appears to be retarded by an excess of alkali. C. S.

Action of Heat on *o*-Aminoazo-compounds. G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1910, **45**, 131—139).—On heating at about 300°, *o*-aminoazo-compounds decompose into triazole, primary amine, and ortho-diamine. This decomposition supports the formula $NH_2{\cdot}Ar{\cdot}N{:}NAr'$ for the *o*-aminoazo-compounds, and is represented by the equation:

$$3NH_2{\cdot}Ar{\cdot}N{:}NAr' = 2Ar{<}\begin{smallmatrix}N\\ |\\ N\end{smallmatrix}{>}NAr' + NH_2Ar' + Ar(NH_2)_2.$$

Thus, tolueneazo-*p*-toluidine yields 2-*p*-tolyl-5-methyl-2 : 1 : 3-benztriazole (compare Zincke, Abstr., 1886, 236), *p*-toluidine, and tolylene-3 : 4-diamine. Benzeneazo-*β*-naphthylamine gives phenylnaphthatriazole (compare Zincke, *loc. cit.*), aniline, and 1 : 2-naphthylenediamine.

p-*Tolueneazo-β-naphthylamine*, $NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4Me$, prepared by the action of *p*-toluenediazonium chloride on *β*-naphthylamine, forms red needles, m. p. 113°. When heated at 300° it decomposes into *p*-toluidine, 1 : 2-naphthylenediamine, and 2-p-*tolylnaphthatriazole*, $C_{10}H_6{<}\begin{smallmatrix}N\\ |\\ N\end{smallmatrix}{>}N{\cdot}C_6H_4Me$, which crystallises in slender, white needles, m. p. 148—149°, and gives a greenish-brown solution in concentrated sulphuric acid. T. H. P.

The Proteins. I. Behaviour of Protein Solutions with Acetone. THEODOR WEYL (*Ber.*, 1910, **43**, 508—511).—Having found that many proteins are precipitated from their solutions by acetone, the author has applied the property to the estimation of the proteins in cow's milk and in fresh bullock's blood, and obtains concordant results. The milk or the blood is diluted with an equal volume of water, and poured into 4 vols. of acetone. The precipitate is collected, washed with equal volumes of acetone and water, then with alcohol, and is finally extracted with ether in a Soxhlet apparatus, dried, and weighed. C. S.

The Isoelectric Constants and the Relative Acidity Constants of Serum-Albumin. LEONOR MICHAELIS and B. MOSTYNSKI (*Biochem. Zeitsch.*, 1910, **24**, 79—91).—From its amphoteric character it can be theoretically deduced from the laws of mass action that the sum of the protein ions is a minimum when the acidity of the solution represents the isoelectric point. This condition can be represented by the equation: $k_a/k_b = [H^{\cdot}]^2/k_w$, where k_a and k_b are the dissociation constants of the protein, functioning respectively as acid and base, and k_w is the dissociation constant of water. This point was experimentally determined by ascertaining the point at which the protein wandered neither to the anode nor cathode in an apparatus arranged according to the following scheme:

Copper in cupric chloride	"Acid mixture" without protein	Acid mixture with 1% protein	Acid mixture without protein	Silver in sodium chloride

The acid mixture was in one set of experiments varying proportions of primary and secondary phosphates, and in the second set, varying proportions of acetic acid and sodium acetate. The isoelectric point was found in one case when the relative amounts of primary to secondary phosphate were as 50 : 1 or $H = 1{\cdot}4\ 10^{-5}$, and in the other case, where the ratio of acetic acid to sodium acetate was between 1 : 2 and 3 : 7 or $H = 1{\cdot}08 \times 10^{-5}$ and $0{\cdot}85\ 10^{-5}$. The above results were obtained with unheated albumin. With heated albumin it was observed that coagulation rapidly took place when the hydrogen ion concentration was near the isoelectric point. The optimum condition for coagulation could be determined with great accuracy, using either of the "acid mixtures" mentioned above. It was found to take place when $[H'] = 0{\cdot}82 \times 10^{-5}$. Theoretical reasons are deduced for believing that the optimum conditions for coagulation correspond with the isoelectric point. From these results it is calculated that the relative acidity constant for ox-serum at 18° is $1{\cdot}1 \times 10^{-4}$. S. B. S.

Putrefaction of Lysine-free Protein. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1910, **64**, 91—94).—Previous experiments have shown that there is reason to believe that arginine is the parent substance of tetramethylenediamine and δ-aminovaleric acid, and that lysine is the parent substance of pentamethylenediamine. On the addition of lysine to a putrefying mixture, the yield of pentamethylenediamine is increased. The present experiments now show that in the putrefaction of gliadin, which is a protein free from lysine, there is no formation of pentamethylenediamine. W. D. H.

The Nature of Oxyhæmoglobin. JOSEPH BARCROFT and A. V. HILL (*J. Physiol.*, 1910, **39**, 411—428).—The velocity of dissociation of oxyhæmoglobin obeys an equation derived from the laws of mass action, and has a high temperature-coefficient, increasing about four times for a rise of 10°. The variations of the equilibrium constant K with change of temperature T follow the equation $\frac{1}{K} \cdot \frac{dK}{dT} = \frac{-q}{2T^2}$, where q is constant and equal to 28,000 calories. From the second law of thermodynamics, q is the heat of combination of 1 gram-molecule of hæmoglobin with oxygen. The amount of heat given out when 1 gram of hæmoglobin unites with oxygen is 1·85 calories. The least possible value for the molecular weight of hæmoglobin in dialysed solution is 16,669. The general conclusion is that hæmoglobin unites chemically with oxygen according to the formula : Hæm. + $O_2 \rightleftharpoons$ Hæm.O_2, and that it is not an adsorption phenomenon. W. D. H.

Modification of Fischer's Ester Method. B. O. PRIBRAM (*Monatsh.*, 1910, **31**, 51—54).—Dry ammonia is employed to liberate the esters of amino-acids from their hydrochlorides. In a preliminary trial, 10 grams of ethyl glycine hydrochloride, dissolved in the smallest necessary quantity of absolute alcohol, were treated with dry ammonia, and, after the addition of dry ether and removal of the ammonium chloride, the solution was evaporated under diminished pressure, the ester was redissolved in alcohol, and the hydrochloride regenerated by

hydrogen chloride; its weight was 6·9 grams, or 69% of the original quantity.

The applicability of the process to the isolation of the products of the hydrolysis of a protein is defined by the following experiment. Dry gelatin is hydrolysed by concentrated hydrochloric acid, the glutamic acid hydrochloride is removed in the usual way, and the filtrate is evaporated to a syrup, which is esterified by the ordinary process of Fischer. After the removal of the ethyl glycine hydrochloride, the filtrate is concentrated under diminished pressure, mixed with dry ether, and saturated with dry ammonia; after about ten minutes, the ether is poured off, replaced by fresh dry ether, and the current of ammonia passed anew, the processes being repeated until the ether remains colourless. The combined ethereal solutions can be directly fractionated, whilst the other products of the hydrolysis can be extracted from the paste of ammonium chloride by means of alcohol. In this way 400 grams of gelatin yield 119·3 grams of esters, whereas by Fischer's process of liberating the esters from the hydrochlorides, 500 grams of gelatin give 117 grams of esters. C. S.

Course of the Hydrolysis of Proteins by Aqueous or Alcoholic Hydrogen Chloride. M. PFANNL (*Monatsh.*, 1910, **31**, 81—85).—Pribram (preceding abstract) has observed that the amount of glycine obtained by the hydrolysis of gelatin by alcoholic hydrogen chloride is very much smaller than that produced when the hydrolysis is effected by hydrochloric acid, and also that the quantities of the esters of amino-acids richer in carbon are about the same in the two processes of hydrolysis. The author now finds that, if care is taken to prevent the hydrolysis of the easily decomposable glycine ester, gelatin yields qualitatively and quantitatively the same products whichever method of hydrolysis is employed. The same is true of the hydrolysis of silk fibroin. C. S.

Comparative Investigations on the Composition and Cleavage of Different Kinds of Silk. VIII. The Mono-amino-acids from Tai-Tsao-Tsam Silk (China). EMIL ABDERHALDEN and JULIUS SCHMID. **IX. The Mono-amino-acids from Chefoo Silk.** E. ABDERHALDEN and ERNST WELDE (*Zeitsch. physiol. Chem.*, 1910, **64**, 460—461, 462—463).—The following table shows the amount of amino-acids in grams per cent. of the two varieties of silk investigated:

	Tai-Tsao-Tsam silk.	Chefoo silk.
Glycine	25·2	12·5
Alanine	18·2	18·0
Leucine	0·9	1·2
Serine	1·2	1·0
Aspartic acid	2·1	2·0
Glutamic acid	2·0	2·0
Phenylalanine	1·0	1·0
Tyrosine	7·8	8·5
Proline	1·0	2·5

W. D. H.

Cataphoresis of Ferments and Colloids. HENRI ISCOVESCO (*Biochem. Zeitsch.*, 1910, **24**, 53—78).—The experiments were carried out in an apparatus, which is figured in the text, consisting essentially of a combination of U-tubes with a central part, which can be shut off from the remainder by glass taps, into which the substance under investigation is introduced. In investigating enzymes, this substance is coagulated egg-white or gelatin, the remainder of the apparatus being filled with enzyme solution. By this arrangement the distance between the electrodes, by means of which the current is introduced, is great, and the effect of electrolysis can be practically eliminated. By determining on which side the ovalbumin or gelatin undergoes alteration, conclusions can be drawn as to the behaviour of the enzymes in an electrical field. By choosing a sufficiently low potential and current strength, appreciable destruction of the enzyme can be avoided. Pepsin wanders towards the negative pole, passes through the ovalbumin on the positive side, and digests it; this can happen before destruction of the enzyme takes place; the latter is affected chiefly by the amount of energy employed (expressed in watts). Similar results with regard to ferment destruction were obtained by the catalase of pigs' liver, which wanders towards the anode. Arsenious sulphide wanders through hardened gelatin towards the positive pole. Similar experiments were performed with colloidal iron, silver, and Magdala-red, and coagulated blood-serum. The result in the last-named case indicated the presence of electropositive and electronegative albumins in the serum. S. B. S.

The Kinetics of Enzyme Actions. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1910, **64**, 82—90. Compare Abstr., 1909, i, 73).—The experiments recorded with trypsin and rennet show that the law of enzyme action is frequently nullified by the presence of inhibiting substances either in the preparation of the enzyme or in the substrate.
W. D. H.

The Question of the Identity of Pepsin and Rennet. W. VAN DAM (*Zeitsch. physiol. Chem.*, 1910, **64**, 316—330).—From the experiments described, it is held that there is no ground for distinguishing a proteolytic from the milk curdling enzyme of the gastric juice. By altering various factors, sometimes the one, sometimes the other action becomes predominant, and the bulk of the paper is concerned with variations in the conditions which lead to such results.
W. D. H.

The Enzymes of Gum Acacia. FRIEDRICH REINITZER (*Zeitsch. physiol. Chem.*, 1910, **64**, 164—168. Compare Abstr., 1909, i, 751).—Polemical. A reply to criticisms by Grafe (this vol., i, 148).
W. D. H.

New Observations on the Individuality of Cellase. GABRIEL BERTRAND and MAURICE HOLDERER (*Compt. rend.*, 1910, **150**, 230—232. Compare this vol. i, 212).—Evidence is adduced in support of the existence of a specific ferment, *cellase*, capable of

effecting the hydrolysis of cellose. The new diastase has been recognised in apricot seeds, in the grains of barley, and in the mycelium of *Aspergillus niger*. It does not appear to occur in blood-serum of horses, in top fermentation yeast, or in glycerol macerations of *Russula queletii*. Partial separation of cellase from emulsin can be effected by taking advantage of the different rates at which the enzymes filter through porcelain. W. O. W.

Method for the Rapid Preparation of Oxidising Enzymes from Plant Extracts. ALEXIS BACH (*Ber.*, 1910, **43**, 362—363).—The addition of 5—10% of magnesium sulphate to a plant extract has the effect of so changing the colloid substances present that they can be easily and quickly precipitated by relatively small quantities of alcohol. Thus, from the extract of *Russula delica*, 5% of magnesium sulphate, followed by alcohol until the solution contained 48%, caused the precipitation of the major part of the impurities. The further addition of alcohol until 70—75% was present, precipitated light-coloured, crystalline substances very rich in oxydases, the last fraction being mainly tyrosinase. The fractions may be freed from magnesium sulphate by dialysis against running water. The precipitates settle rapidly, and the whole process only takes three to four hours.
E. F. A.

Theory of the Action of Oxydases. I. Oxydases free from Manganese and Iron. ALEXIS BACH (*Ber.*, 1910, **43**, 364—366).—Bertrand (Abstr., 1898, i, 53; ii, 128) has suggested that oxydases are to be regarded as organic manganese compounds. Others have prepared active oxydases containing iron instead of manganese, whilst the peroxydases (Bach and Tscherniac, Abstr., 1908, i, 746) have been proved to contain neither metal. Active oxydase preparations have now been obtained from *Lactarius vellereus* and *Russula delica* by precipitation with 65—75% alcohol, after the addition of magnesium sulphate (see preceding abstract), which are absolutely free from either manganese or iron. E. F. A.

Theory of the Action of Oxydases. II. Influence of Metallic Salts on the Subsequent Change of the Products of Oxydase Action. ALEXIS BACH (*Ber.*, 1910, **43**, 366—370).—Metallic salts do not take part in the primary oxidation of tyrosine and phenols by tyrosinase or phenolase, that is, the absorption and activation of the oxygen, but they very greatly accelerate the further change of the primary oxidation products. Thus a tyrosine solution coloured deep red by the action of tyrosinase becomes violet and then black in a few minutes on the addition of aluminium sulphate, and the characteristic black precipitate soon forms. Aluminium sulphate similarly accelerates the formation of purpurogallin from the yellow product formed by the action of oxydase on pyrogallol.

Metallic salts also indirectly accelerate the actual oxydase action when they facilitate the removal of products of the action which are acting to stop the oxydase. This explanation applies to the accelerating action of manganese salts on the oxidation of drying oils and

quinol. Oxydase action is to be regarded as a process taking place in two phases, and brought about by the agency of two kinds of catalyst. The molecular oxygen is activated by the oxygenase, forming peroxide, whilst the peroxydase brings about the transference of the labile peroxide oxygen to the substrate. In the case of phenolase, the peroxydase can be replaced by metallic salts, but with tyrosine the metallic salts are not replaceable by peroxydase. E. F. A.

Formation of Phosphates in Alcoholic Fermentation. ARTHUR HARDEN and WILLIAM J. YOUNG (*Centr. Bakt. Par.*, 1910, ii, **26**, 178—184. Compare Abstr., 1908, i, 590).—The formation of hexose phosphate is accompanied by an exactly equivalent amount of alcoholic fermentation, and does not precede the alcoholic fermentation as required by Iwanoff's theory (Abstr., 1909, i, 752).

The loss of fermenting power caused by washing zymin with water is shown to be due to the removal of the soluble co-enzyme. There is no experimental evidence that Iwanoff's synthease exists.

N. H. J. M.

Transformation of Aromatic Alcohols into Phosphinous Acids by Hypophosphorous Acid. ROBERT FOSSE (*Compt. rend.*, 1910, **150**, 178—180; *Bull. Soc. chim.*, 1910, [iv], **7**, 228—231. Compare Abstr., 1906, i, 691, 975; 1907, i, 414; 1908, i, 567).—Certain aromatic alcohols react with hypophosphorous acid with the elimination of water and the formation of a substituted acid; simultaneously, a portion of the alcohol undergoes reduction to the corresponding hydrocarbon. Thus triphenylcarbinol forms triphenylmethane and *triphenylmethylphosphinous acid*, $CPh_3\cdot PHO\cdot OH$. Dinaphthapyranol forms dinaphthapyran and *dinaphthapyrylphosphinous acid*, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot PHO\cdot OH$ Michler's carbinol forms the corresponding hydrocarbon and the *acid*, $CH(C_6H_4\cdot NMe_2)_2\cdot PHO\cdot OH$.

When the corresponding aldehydes or ketones are treated with hypophosphorous acid, additive compounds are formed of the type

$R\cdot CH(OH)\cdot PHO\cdot OH$. W. O. W.

Preparation of an Arsenic-albumin Compound. FRIEDR. AUGUST VOLKMAR KLOPFER (D.R.-P. 214717).—When the nuclein-free vegetable albumin obtained from wheat is treated with arsenious chloride in the presence of a diluting agent, reaction takes place at the ordinary temperature. The *arseno-albumin* so obtained is readily soluble in water, but insoluble in the gastric juice; it contains N = 12·95%, S = 1·78%, Cl = 4·72%, and As = 4·33%. F. M. G. M.

Organic Chemistry.

Some Fluoro-derivatives of Methane. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1910, 113—123).—When bromoform (3 mols.) is heated with antimony trifluoride and bromine in a platinum reflux apparatus for twenty-four hours at 110—120°, one atom of bromine is substituted by fluorine. If double the proportion of antimony trifluoride is used and the heating continued for seventy-two hours, two atoms of bromine are replaced, but the latter reaction does not occur to any appreciable extent until the former is complete.

Fluorodibromomethane, $CHFBr_2$, the product of the first reaction, is a colourless liquid, b. p. (corr.) 64·9°/757 mm., $D^{18·5}$ 2·4256, which becomes slightly yellow when exposed to the light. It is slowly decomposed on exposure to light and moist air, with the formation of hydrogen fluoride and bromide. Fluorodibromomethane is reduced by zinc dust in alcoholic solution at 70° with the production of methylene fluorobromide, methyl fluoride, and hydrogen. That the latter is formed by the catalytic dehydrogenation of the alcohol is shown by the presence of aldehyde in the alcoholic solution. Fluorodibromomethane is attacked by sodium ethoxide with the formation of sodium formate.

Difluorobromomethane, $CHBrF_2$, the product of the second of the above reactions, is a gas, b. p. $-14·5°$, $D^{15·7}$ 4·53—4·57 (air = 1), soluble in half its volume of water at 18°, and in one-thirty sixth of its volume of alcohol at 17°. When passed over soda-lime it is decomposed, approximately two-fifths being converted into carbon monoxide, and the remainder into formate. The reaction, very rapid at first, about 70% of the total change occurring in the first thirty minutes, afterwards slackens, and requires nine days for completion. Concentrated aqueous potassium hydroxide solutions act similarly. An ethereal solution of difluorobromomethane is not attacked by sodium at the ordinary temperature. When an absolute alcoholic solution of the gas (1 mol.) at $-15°$ is treated with a solution of potassium ethoxide (1 mol.) in the same solvent at the same temperature, the product consists of unchanged substance, potassium formate, slight amounts of potassium fluoride and bromide, and a small quantity of a *liquid*, b. p. 45—50°, insoluble in water, which seems to be ethyl difluoromethyl ether, $CHF_2·OEt$, isomeric with the difluoroethyl methyl ether described previously (Abstr., 1902, i, 129). An attempt to replace the hydrogen atom in difluorobromomethane by mercury by treatment with an alkaline solution of mercuric cyanide was also unsuccessful.

It has been shown previously (Abstr., 1898, i, 457) that the replacement of bromine by fluorine in the halogen compounds containing C_2 causes a depression in the boiling points of about 63°. It is now found that in the methane series the corresponding

depression is almost constantly 80°. The corresponding lowering of the boiling points of the chloro-derivatives by substitution of fluorine is about 44° in compounds containing C_2, and 50° in the methane series respectively. E. H.

Non-dehydration of Hydrates by Absolute Alcohol. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1910, **7**, 211—216).—Absolute alcohol extracts the water of crystallisation from the hydrates $BaCl_2,H_2O$; $BaCl_2,2H_2O$, and $Li_3SbS_4,10H_2O$, but not from $CuCl_2,2H_2O$ and $CuSO_4,H_2O$. A. J. W.

Mechanism of Catalytic Dehydration of Alcohols by Different Metallic Oxides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, **150**, 823—826. Compare Abstr., 1908, i, 594, 713; 1909, i, 546).—The following equations are put forward to account for the catalytic dehydration of alcohols by thorium oxide: (1) $ThO_2 + 2C_nH_{2n+1}\cdot OH = ThO(OC_nH_{2n+1})_2 + H_2O$. (2) Below 300°: $ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_nH_{2n+1})_2O$. (3) Above 300°:

$$ThO(OC_nH_{2n+1})_2 = ThO_2 + H_2O + 2C_nH_{2n}.$$

The catalytic formation of amines (Abstr., 1909, i, 292) may similarly be explained by the interaction of the unstable thorate and ammonia. It might be expected that the action of hydrogen sulphide on the thorate would lead to the formation of thiols; experiments have verified this prediction, and led to the discovery of a new general method for the synthesis of these substances.

W. O. W.

Autoxidation of Aliphatic Amino- and Polyhydroxy-derivatives. WILHELM TRAUBE (*Ber.*, 1910, **43**, 763—772).—It has been shown previously that aqueous solutions of amines and amino-acids are capable of dissolving copper powder in the presence of oxygen, the products being aldehydes and ammonia (Abstr., 1906, i, 143). It is now shown that aqueous solutions of polyhydroxy-compounds, such as ethylene glycol, glycerol, or mannitol, are capable of dissolving copper in the presence of oxygen, and that the product of oxidation in each case is formic acid. It has been proved that carbonic acid is not formed during the oxidation. The absorption of oxygen takes place more rapidly when copper wool is used in place of turnings.

Oxygen is also absorbed when an alkaline solution of cupric hydroxide is used instead of metallic copper, but in this case it is advisable to work at a temperature of 60—70°.

Fehling's solution also absorbs oxygen, yielding formic acid. Solutions of cupric hydroxide in methylamine or in alkaline solutions of glycine absorb oxygen at 60°, yielding formaldehyde in the first case and oxalic acid in the second.

In all these reactions, the absorption of oxygen and the oxidation of the ammonia, amine, or hydroxy-compound proceed more readily when metallic copper is present and goes into solution. If cupric hydroxide is used, a higher temperature is required. This may be due to the fact that the oxidation and solution of the copper produce

local raising of the temperature, which accelerates the oxidation of the organic compound; when a solution of copper hydroxide is used, no internal heating takes place, and hence the need of external heating.

In all cases the reaction is regarded as an oxidation of complex copper compounds, for example, with ammonia of the compound

$$Cu(NH_3)_2(OH)_2,$$

and in all cases a certain minimum concentration of hydroxyl ions is necessary. It is possible that the copper of the complex compound takes up oxygen, yielding a copper peroxide derivative, and that the oxygen is then transferred to the amino- or hydroxy-portion of the complex molecule. J. J. S.

[**Oxidation of Unsaturated Compounds by means of Organic Peroxides.**] NIKOLAUS PRILESCHÉEFF (*Ber.*, 1910, **43**, 959. Compare this vol., i, 86).—A reply to Lippmann's claim for priority (this vol., i, 149). C. S.

Organic Compounds Spontaneously Oxidisable with Phosphorescence. MARCEL DELÉPINE (*Compt. rend.*, 1910, **150**, 876—878. Compare Abstr., 1902, i, 271, 595, 597, 702; 1903, i, 237).—Dithiocarbonic esters of the type OR·CS·SR′, and thiocarbamic esters of the type NR_2·CS·OR′, fume in the air at the ordinary temperature, emitting vapours which appear luminous in the dark. The ester, $CS(OMe)_2$, shows the same phenomenon. Phosphorescence, which is due to oxidation, varies in a marked manner with the volatility of the compounds, those members of the series having relatively low boiling points being the most luminous. The phosphorescence appears to be associated with the presence of the $S\!:\!\dot{C}\cdot O-$ group in the molecule.

W. O. W.

Lipoids. IX. Sahidin from Human Brain. SIEGMUND FRÄNKEL and KURT LINNERT (*Biochem. Zeitsch.*, 1910, **24**, 268—276).—The substance to which the authors give the name sahidin was prepared in the following way. To the concentrated extract made with light petroleum was added alcohol to precipitate the kephalin. After concentration, alcoholic lead acetate, made weakly alkaline with ammonia, was added. The excess of ammonia was distilled off, and the excess of lead precipitated by alcoholic hydrogen chloride, the latter being added until the solution was just acid to Congo paper. Cadmium chloride in alcoholic solution was then added, and the precipitate thus formed was extracted with hot benzene; from the latter solution, the cadmium salt of sahidin was precipitated, and was purified, after washing with alcohol, ether, and cold benzene, by solution again in hot benzene, and re-precipitation by alcohol. The analysis corresponds with the formula $C_{80}H_{167}O_{12}N_3Cl_6P_2Cd_3$. The substance is dextrorotatory andunsaturated (iodine number 34), and has only one methyl group combined with nitrogen. Only one atom of nitrogen, therefore, is in the form of choline, which was isolated both by acid hydrolysis and hydrolysis by barium hydroxide; a lævorotatory glycerophosphoric acid was also produced from the substance by hydrolysis. S. B. S.

A Comparison between the Properties of Protagon and the Properties of a Mixture of Phosphatides and Cerebrosides. WILHELM CRAMER (*Quart. J. exp. Physiol.*, 1910, 3, 129—138).—Polemical. W. D. H.

Ferriacetates, the Acetic Acid Reaction with Ferric Chloride, and the Basic Precipitation of Iron. RUDOLF F. WEINLAND and ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1910, 66, 157—168. Compare Abstr., 1909, i, 757).—A solution of ferric chloride (1 mol.) and sodium acetate (3 mols.) contains the hexa-acetotriferri-base previously described, the platinichloride of which is precipitated on the addition of sodium platinichloride. The red colour of such a solution is due to the presence of the mono-acetate, $\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]\cdot OAc$, and not to that of an undissociated acetate, $Fe(OAc)_3$. It has not been found possible to prepare a triacetate of the base.

The precipitate obtained when a solution containing ferric chloride and sodium acetate is boiled, corresponds approximately with the composition: $\left|Fe_3\begin{matrix}OAc\\(OH)_2\\O_3\end{matrix}\right|$.

The diacetate of the triferri-base is most readily prepared by dissolving the mono-acetate in hot glacial acetic acid, and distilling off the acetic acid at 130—140°. The salt forms rectangular, brick-red tablets. C. H. D.

Compounds with a Branched Chain. MLLE. GERMAINE FREYLON (*Ann. chim. Phys.*, 1910, [viii], 19, 551—574).—Henri (*Jahresberichte*, 1889) has described the preparation of ethyl α-cyano-γ-methylvalerate by the action of *iso*butyl bromide on ethyl sodiocyanoacetate; repetition of his experiments, however, has shown that the sole product of the reaction is *ethyl α-cyano-γ-methyl-α-*iso*butylvalerate*, $C_{13}H_{23}O_2N$, b. p. 132°/15 mm. An unexpected result follows when this substance is reduced with sodium and absolute alcohol, three compounds being obtained: (1) α-*iso*butylvaleric acid; (2) *δ-methyl-β-*iso*butylamylamine*, $CH_2Pr^\beta\cdot CH(CH_2Pr^\beta)\cdot CH_2\cdot NH_2$, b. p. 85—86°/18 mm.; the *carbamide* has m. p. 84—85°; the *phenylcarbamide* has m. p. 123°; (3) *α-cyano-γ-methyl-α-*iso*butylvaleric acid*, $CO_2H\cdot C(CH_2Pr^\beta)_2\cdot CN$, m. p. 90—91°; when this is heated, carbon dioxide is lost, and *γ-methyl-α-*iso*butylvaleronitrile*, $CH(CH_2Pr^\beta)\cdot CN$, is formed. The latter has b. p. 90—91°/15 mm., D_0^4 0·825; reduction leads to the formation of the foregoing amine, and when the substance is heated at 140° with sodium and the product treated with water, βζ-dimethylheptane is formed, together with di*iso*butyl ketone. The ketone, which has also been prepared from di*iso*butylcarbinol, forms a *semicarbazone*, m. p. 116—117°, and an *oxime*, b. p. 104—106°/10 mm., the *carbanilide* of which has m. p. 91—92°. Di*iso*butylcarbinol, b. p. 81—82°/18 mm., has not hitherto been obtained pure (Grignard, Abstr., 1901, i, 250); it forms a *phenylurethane*, m. p. 61—62°, and a *pyruvate*, b. p. 118—120°/18 mm., the *semicarbazone* of which has m. p. 114—115°. W. O. W.

Fatty Acids in Cod Liver Oil. A. HEIDUSCHKA and E. RHEINBERGER (*Pharm. Zentr.-h.*, 1910, **51**, 203—204).—A solution in chloroform of the fatty acids, obtained by hydrolysing cod liver oil from the torsk with alcoholic potassium hydroxide and subsequent acidification, is treated with Hübl's iodine solution and kept in darkness for two days, whereby a sparingly soluble crystalline *powder*, $C_{17}H_{26}O_2Cl_4I_4$, is obtained, which is probably a derivative of terapic acid. Submitted to the action of dry chlorine at about 50° for ten hours, the powder is converted into an *octachloride*, $C_{17}H_{26}O_2Cl_8$, m. p. 62°. C. S.

Preparation of Glycerol Mono- and Di-lactates. KALLE & Co. (D.R.-P. 216917).—*Glycerol monolactate* is formed when an adequate mixture of glycerol and lactic acid is slowly heated to 150—160° and the product distilled in a vacuum; it is a viscous, colourless, hygroscopic syrup. *Glycerol dilactate* is prepared in the same way, and has similar properties; these compounds are also obtained when sodium, potassium, or silver lactate is heated with dichlorohydrin; they are sparingly soluble or insoluble in organic solvents; miscible with water or alcohol, in which they decompose slowly at the ordinary temperature, rapidly on heating; and are employed therapeutically as lactic acid substitutes. F. M. G. M.

Etholides from Coniferæ. Juniperic and Sabinic Acids. J. BOUGAULT (*Compt. rend.*, 1910, **150**, 874—876.* Compare Abstr., 1909, i, 82).—The constitution of juniperic and sabinic acids, recently obtained from the waxes of certain Coniferæ, has now been established. Sabinic acid is λ-hydroxylauric acid, since its iodo-derivative yields lauric acid on reduction, whilst oxidation of the acid gives Noerdlinger's decamethylenedicarboxylic acid (Abstr., 1890, 1237). Similarly, juniperic acid is *o*-hydroxypalmitic acid, since palmitic acid was obtained by reducing the iodo-derivative, and oxidation gave a tetradecamethylenedicarboxylic acid, identical with Canzoneri's thapsic acid (Abstr., 1883, 460).

The following derivatives are described: o-*iodopalmitic acid*,

$$CH_2I\cdot[CH_2]_{14}\cdot CO_2H,$$

m. p. 76°; λ-*iodolauric acid*, $CH_2I\cdot[CH_2]_{10}\cdot CO_2H$, m. p. 63—64°; *ethyl tetradecamethylenedicarboxylate*, $CO_2Et\cdot[CH_2]_{14}\cdot CO_2Et$, m. p. 39°. W. O. W.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc. II. Preparation of Aliphatic Ketonic Acids. I. EDMOND É. BLAISE and A. KŒHLER (*Bull. Soc. chim.*, 1910, [iv], **7**, 215—227).—An account, with further experimental details, of compounds obtained by the methods already described (Abstr., 1909, i, 204).

Ethyl hydrogen adipate, $C_8H_{14}O_4$, is crystalline, and has m. p. 29°, b. p. 160°/7 mm., 180°/19 mm.; the *anilide*, prepared from the acid chloride, crystallises in needles, m. p. 45°; the *a-naphthylamide* forms slender needles, m. p. 75°. The *chloride*, $CO_2Et\cdot[CH_2]_4\cdot COCl$, has b. p. 117—118°/9 mm., 128°/17 mm.

* and *J. Pharm. Chim.*, 1910, [vii], **1**, 425—432.

Ethyl hydrogen pimelate, $C_9H_{16}O_4$, has m. p. 10°, b. p. 182°/18 mm., and forms a p-*toluidide*, m. p. 92°, and a *chloride*, b. p. 139°/17 mm.; diethyl pimelate has b. p. 144°/16 mm.

Ethyl hydrogen suberate, $C_{10}H_{18}O_4$, occurs in spherular crystals, m. p. 25°, b. p. 192°/17 mm., and forms a p-*toluidide*, m. p. 74°, and a *chloride*, b. p. 143°/15 mm.

ε-Ketoheptoic acid, prepared by treating ethyl adipyl chloride with zinc methyl iodide (compare Perkin, Trans., 1890, **57**, 229), forms a *semicarbazone*, m. p. 144°; the *ethyl* ester, b. p. 120·5°/11 mm., forms a *semicarbazone*, m. p. 107°.

ε-Keto-octoic acid, m. p. 52°, b. p. 160—161°/9 mm., gives a green *copper* salt, a crystalline *calcium* salt, $C_{16}H_{26}O_6Ca,H_2O$, and a *semicarbazone*, m. p. 190°; the *methyl* ester has b. p. 122—123°/14 mm.; the *ethyl* ester, b. p. 125°/12 mm., forms a *semicarbazone*, m. p. 88·5°.

ε-Ketononoic acid gives a *copper* salt, a *potassium* salt,

$$C_9H_{15}O_3K,8H_2O,$$

a *semicarbazone*, m. p. 169°, and a *methyl* ester, b. p. 143°/21 mm.; the *ethyl* ester, b. p. 153°/21 mm., forms a *semicarbazone*, m. p. 85°.

The *nickel*, *mercury*, *potassium*, and *lead* salts of η-ketodecoic acid, m. p. 64°, are described; the *semicarbazone* has m. p. 184°; the *ethyl* ester, b. p. 157°/15 mm.

γ-Keto-octoic acid, m. p. 53°, furnishes a *semicarbazone*, m. p. 153°, a p-*nitrophenylhydrazone*, m. p. 152°, a *methyl* ester, b. p. 111°/15 mm., an *ethyl* ester, b. p. 125°/15 mm., and *copper*, *calcium*, and *zinc* salts, the two latter crystallising with $1H_2O$. W. O. W.

Some Derivatives of Mesoxalic Acid. H. Filippo, jun. (*Rec. trav. chim.*, 1910, [ii], **14**, 113—129).—Sodium tartronate is conveniently obtained by heating sodium dihydroxytartrate to 100—120°. *Methyl tartronate* has m. p. 44·5—45°, and b. p. 122°/19 mm. Ethyl tartronate has m. p. 2·5° and b. p. 120·5—121°/15 mm. At atmospheric pressure the substance cannot be distilled without decomposition; this explains the contradictions found in the literature as to its b. p. *Tartronodi-methylamide*, $OH{\cdot}CH(CO{\cdot}NHMe)_2$, has m. p. 153—154°. Methyl mesoxalate and ethyl mesoxalate can be prepared with almost quantitative yields by the action of bromine on the corresponding tartronates (compare Conrad and Brückner, Abstr., 1892, i, 40). When an alcoholic solution of ethyl mesoxalate is treated with an alcoholic solution of ammonia, a *substance* is precipitated which readily loses ammonia, and is not the expected amide. If the substance is treated with a dilute methyl-alcoholic solution of hydrochloric acid, ammonium chloride is precipitated, and the solution on evaporation yields mesoxalamide. The amide can be obtained pure only in this way (compare Petriew, Abstr., 1878, 490). Jaeger.—The large, colourless, transparent crystals are rhombic-pyramidal: $a : b = 0{\cdot}8947 : 1$ ($b : c$ could not be determined). Ethyl acetoxymalonate has m. p. 68° (Petriew, *loc. cit.*, gave 145°). R. V. S.

Zinc Formaldehydesulphoxylate. Wilh. Becker (*Ber.*, 1910, **43**, 856—857. Compare Bazlen, this vol., i, 40).—The di-zinc salt of formaldehydesulphoxylic acid is readily prepared by saturating a

cold mixture of 80 grams of zinc dust (90%) and 400 grams of water with sulphur dioxide, and then adding the requisite amount of formaldehyde solution. The zinc slime is removed, and the filtrate kept at the ordinary temperature for six to eight days, when crystals of the pure salt, $ZnSO_2,CH_2O,H_2O + 2H_2O$, separate.

When the filtrate is warmed for an hour on the water-bath, the compound $ZnSO_2,CH_2O,H_2O$ is obtained as minute rhombohedra.

J. J. S.

Action of Bases on Chloral Hydrate. J. E. Enklaar (*Rec. trav. chim.*, 1910, [ii], **14**, 173—184. Compare Abstr., 1905, i, 170, 741).—Continuing his study of the above reaction, the author confirms his former statement that it is unimolecular in dilute solutions at 0°. At higher temperatures (15°, 20°, 30°) it is slower than the molecular formula would require, but the constants at these temperatures do not approximate to those of a bimolecular reaction. This behaviour (as also the results of Böttger and Kötz, Abstr., 1902, i, 659, and even of Werner, Trans., 1904, **85**, 1376) is explained by the supposition that a salt of chloral hydrate is formed and undergoes partial hydrolysis, the extent of which will depend largely on the temperature. R. V. S.

Stability of β-Ketonic Aldehydes. François Couturier (*Compt. rend.*, 1910, **150**, 705—706. Compare Abstr., 1905, i, 570).—Condensation of ζ-methylheptan-β-one with ethyl formate in presence of sodium leads to the formation of an unstable *methyloctanal*, which has been isolated in the form of its *copper* derivative, $(C_9H_{16}O_2)_2Cu$, m. p. 112°. ζ-Methylhepten-β-one does not condense with ethyl formate.

iso*Propylideneacetoacetaldehyde*, $CMe_2\colon CH\cdot CO\cdot CH\colon CH\cdot OH$, is obtained from mesityl oxide. The *copper* salt occurs in black crystals, m. p. 134°; the aldehyde undergoes decomposition when distilled. n-*Butyleneacetoacetaldehyde*, $CH_2\colon CH\cdot[CH_2]_2\cdot CO\cdot CH\colon CH\cdot OH$, prepared from allylacetone, forms a blue, crystalline *copper* salt, m. p. 136°; the free aldehyde has b. p. 58°/13 mm. with slight decomposition.

The stability of β-ketonic aldehydes diminishes as the ethylenic linking approaches the ketonic group. W. O. W.

Chemical Action of Light. XVI. Giacomo Ciamician and Paul Silber (*Ber.*, 1910, **43**, 945—949; *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 364—367).—A mixture of acetone and methyl alcohol, in the proportion 1 : 2, is exposed to light for a very long time, and is then distilled on the water-bath and, finally, with steam; the residue is found to consist of *iso*butylene glycol. Acetone and ethyl alcohol, after exposure to light during the summer and autumn months, leave, after the removal of the portions volatile with steam, a liquid which, despite its constant b. p., 177°, is certainly a mixture, one constituent of which is *iso*amylene βγ-glycol, since treatment with hot dilute sulphuric acid results in the formation of methyl *iso*propyl ketone (semicarbazone, m. p. 112°).

The prolonged action of light on a mixture of acetone and benzyl alcohol results, not in the formation of an additive compound as in the two preceding cases, but in the oxidation of the alcohol, dihydrobenzoin and *iso*dihydrobenzoin being produced. C. S.

Alkylation of Aliphatic Ketones by the Use of Sodamide. Fission of Hexa-alkylacetones. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1910, **150**, 661—667. Compare Abstr., 1904, i, 600).—When aliphatic ketones are alkylated by the method already described, the ultimate product is a hexa-alkylacetone of the type CRR′R″·CO·CRR′R″. When such a compound is boiled with sodamide in presence of an aromatic hydrocarbon, decomposition occurs, with production of an aliphatic hydrocarbon and a trialkylacetamide, unless the ketone is unsymmetrical, when two hydrocarbons and two amides are obtained (compare Abstr., 1909, i, 131, 654).

When methyl iodide is boiled in ethereal solution with the product of the action of diethyl ketone on sodamide, the mixture contains ethyl *iso*propyl ketone, di*iso*propyl ketone, and a *compound*, $C_{15}H_{26}O$, b. p. 148—152°/18 mm. The action of ethyl iodide on the sodium derivative of di*iso*propyl ketone leads to the formation of *βδδ-trimethylhexan-γ-one*, $CHMe_2$·CO·CMe_2Et, b. p. 158—161°; on reduction this yields *βδδ-trimethylhexan-γ-ol*, $C_9H_{20}O$, b. p. 170—171°; the *phenylurethane* has m. p. 164°. *γγεε-Tetramethylheptan-δ-one*, CMe_2Et·CO·CMe_2Et, prepared in the same way, has b. p. 196—198°; *γγεε-tetramethylheptan-δ-ol*, $C_{11}H_{24}O$, has b. p. 210—212°, and forms a *phenylurethane*, m. p. 62—63°.

When ββδδ-tetramethylpentan-γ-one is boiled with benzene and sodamide, β-methylpropane is formed, together with ββ-dimethylpropionamide. Under the same conditions, the unsymmetrical compound, ββδδ-tetramethylhexan-γ-one, yields the same substances, and also β-methylbutane and αα-dimethylbutyramide. The reaction follows a parallel course with γγεε-tetramethylheptan-δ-one and ββδδ-tetramethylhexan-γ-one (compare this vol., i, 219). W. O. W.

Isolation of a Biose Derived from Amygdalin. JEAN GIAJA (*Compt. rend.*, 1910, **150**, 793—796. Compare Auld, Trans., 1908, **93**, 1251—1276; Armstrong, Abstr., 1908, i, 741).—At the commencement of the hydrolysis of amygdalin by the digestive juice of *Helix pomatia*, the reducing power of the sugar produced is one-quarter to one-third of that required by the hypothesis that a reducing disaccharide is formed. The reducing properties of the solution are entirely due to dextrose, but a biose is formed as an intermediate product, and has now been isolated. The substance has been obtained as an amorphous powder, insoluble in alcohol, but very soluble in water; it does not undergo fermentation by yeast, but is readily hydrolysed by the juice of snails, dextrose being the only product. The suggestion is put forward that the compound has a constitution resembling that of trehalose. W. O. W.

Influence of Salts on the Optical Rotatory Power of Sucrose and Raffinose. EDWARD W. WASHBURN (*Zeitsch. Ver. deut. Zuckerind*, 1910, 381—385).—The measurements were made with a high degree of accuracy, using specially purified materials. Sodium chloride slightly diminishes the rotatory power of sucrose

according to the formula: $[\alpha]_D^{25} = 66.41° - 1.456R$, where R is the ratio of the amount of salt to that of sucrose present.

The rotatory power of raffinose is very slightly increased by sodium, potassium, or lithium chlorides. The influence of lithium chloride, tested at three different concentrations, is linear. E. F. A.

Coagulation of Starchy Material by Freezing. GIOVANNI MALFITANO and Mlle. A. MOSCHKOFF (*Compt. rend.*, 1910, **150**, 710—711).—When a 2% solution of potato starch is cooled, a coagulum separates, whilst the residual liquid retains most of the mineral matter, together with some starch. If the coagulum is washed and the operation repeated, the liquid is found to contain only traces of starch and mineral matter. The process affords, therefore, a convenient method for purifying starchy materials. The quantity of starch remaining in the residual liquid appears to depend on the amount of electrolytes present.

The author considers that his experiments support the view put forward (Abstr., 1906, i, 804) to explain the condition of starch molecules in colloidal solutions. W. O. W.

Hydrolysis of Cellulose with Hydrofluoric Acid. JULES VILLE and W. MESTREZAT (*Compt. rend.*, 1910, **150**, 783—784).—Dilute hydrofluoric acid (5—30%) has little effect on cellulose. More concentrated acid brings about destructive hydrolysis. By heating on the water-bath with the 50% acid for six hours, a 50% yield of dextrose is obtained. W. O. W.

Degradation of Cotton Cellulose. CARL G. SCHWALBE and W. SCHULZ (*Ber.*, 1910, **43**, 913—917).—Guignet's soluble cellulose (Abstr., 1889, 847) is exceedingly resistant to hydrolysis. When boiled with dilute sulphuric acid, the reducing power decreases, indicating reversion. It is stable at 105°, dissolves to the extent of 70% in 10% alkali hydroxide, and only gives a coloration with iodine solution on the addition of sulphuric acid. More concentrated sulphuric acid converts it into a substance showing a higher reducing power than "parchment," and differing also from the latter in resisting hydrolysis. Flechsig's amyloid is also different from "parchment"; it is completely soluble in 10% alkali hydroxide, decomposes at 105°, and only shows a coloration with iodine in presence of sulphuric acid. Ekström's acid cellulose is characterised by the great increase in the reducing power on hydrolysis, and the coloration with iodine in the absence of sulphuric acid.

By the action of 69% sulphuric acid on cellulose, 20% of dextrose was obtained, partly crystalline, partly as phenylosazone. To obtain satisfactory yields, the acid should be neutralised with barium carbonate and not with sodium hydroxide. By Ekström's process 44% of dextrose was obtained. The largest amount of dextrose was obtained in experiments showing only very small reducing power. The reducing power was much increased, however, when barium carbonate was substituted for sodium hydroxide to neutralise the acid.

A mixture of dextrose and Guignet's soluble cellulose shows a lower reducing power than the sum of the reducing powers of the components. In hydrolysis when the reducing power is high, possibly the crystallisation of the dextrose is hindered by the by-products, or these by-products (dextrins) have themselves a high reducing power, and this reduction is an indication of incomplete hydrolysis. On the other hand, when the reducing power of the hydrolysed mixture is low, the true reducing power of the sugar present is to some extent masked by the formation of loose compounds with the by-products. These are destroyed by neutralisation and evaporation, as the dextrose can then be caused to crystallise. E. F. A.

Behaviour of Cellose towards Certain Enzymes. EMIL FISCHER and GÉZA ZEMPLÉN (*Annalen*, 1910, **372**, 254—256. Compare Abstr., 1909, i, 209).—The authors confirm the observation of Bertrand and Holderer (compare this vol., i, 212) that cellose is hydrolysed by the enzymes of *Aspergillus niger*. It is also found that cellose is hydrolysed slowly by an extract of Kephir. W. H. G.

Crystallographic Properties of Some Compounds of Ethylenediamine. MAX FRANK (*Zeitsch. Kryst. Min.*, 1910, **47**, 346—362). —The following compounds have been examined crystallographically: Diethylenediaminecopper chloride, $Cu[en_2]_2Cl_2,2H_2O$, monoclinic [$a:b:c = 0·3917:1:0·82724$; β 110°30′], and the bromide, $Cu[en_2]_2Br_2,2H_2O$, monoclinic [$a:b:c = 0·41831:1:0·83415$; β 111°45′]. Triethylenediaminenickel chloride, $Ni[en_2]_3Cl_2,2H_2O$, rhombic [$a:b:c = 0·68598:1:1·0557$], and the bromide, $Ni[en_2]_3Br_2,2H_2O$, rhombic [$a:b:c = 0·7299:1:1·0604$]. The members of each of the preceding pairs are isomorphous, as also are the following: Triethylenediaminezinc chloride, $Zn[en_2]_3Cl_2$, rhombic [$a:b:c = 0·6236:1:0·9482$], the bromide, $Zn[en_2]_3Br_2$, rhombic [$a:b:c = 0·74946:1:1·21430$], and the iodide, $Zn[en_2]_3I_2$, rhombic [$a:b:c = 0·53282:1:0·8977$]. Triethylenediaminecadmium bromide, $Cd[en_2]_3Br_2$, rhombic [$a:b:c = 0·69718:1:1·1014$], and the iodide, $Cd[en_2]_3I_2$, rhombic [$a:b:c = 0·7864:1:1·0212$]. Triethylenediaminecadmium sulphate, $Cd[en_2]_3SO_4$, rhombic [$a:b:c = 0·57735:1:x$], and the zinc salt, $Zn[en_2]_3SO_4$. The following are also described: Diethylenediaminecopper nitrate, $Cu[en_2]_2(NO_3)_2,2H_2O$, monoclinic [$a:b:c = 1·3034:1:0·7997$; β 110°49′]. Triethylenediaminecopper thiocyanate, $Cu[en_2]_3(SCN)_2,5H_2O$, rhombic [$a:b:c = 0·46807:1:0·65231$]. Ethylenediaminecopper acetate, $Cu[en_2](C_2H_3O_2)_2,H_2O$, monoclinic [$a:b:c = 0·9556:1:1·3396$; β 107°49′]. Triethylenediaminenickel iodide, $Ni[en_2]_3I_2,H_2O$, rhombic [$a:b:c = 0·9195:1:0·5486$]. Triethylenediaminenickel thiocyanate, $Ni[en_2]_3(SCN)_2$, monoclinic [$a:b:c = 1·071:1:0·6087$; β 95°32′]. Diethylenediaminenickel cyanide, $Ni[en_2]_2(CN)_2$, rhombic [$a:b:c = 0·78036:1:0·5840$]. Triethylenediaminezinc thiocyanate, $Zn[en_2]_3(SCN)_2$, monoclinic [$a:b:c = 0·9992:1:0·6749$; β 103°16′]. Diethylenediaminecadmium thio-

cyanate, $Cd[en_2]_2(SCN)_2$, monoclinic [$a:b:c=1·1469:1:1·1145$; β 109°45′]. Ethylenediammoniumzinc thiocyanate,

$$Zn[C_2H_4N_2H_6](SCN)_4,4H_2O,$$

monoclinic [$a:b:c=2·023:1:0·9497$; β 100°7′]; the cadmium salt, $Cd[C_2H_4N_2H_6](SCN)_4$, monoclinic [$a:b:c=1·0313:1:1·0628$; β 108°36′]. Ethylenediammoniumzinc sulphate, $Zn[C_2H_4N_2H_6](SO_4)_2,6H_2O$, monoclinic [$a:b:c=0·74897:1:0·49606$; β 107°22′]. C. S.

Preparation of β-Methyltetramethylenediamine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 216808).—The conversion of β-methyladipodiamide,

$$NH_2·CO·CH_2·CHMe·CH_2·CH_2·CO·NH_2,$$

into $\alpha\delta$-diamino*iso*pentane, $NH_2·CH_2·CHMe·CH_2·CH_2·NH_2$, has previously been accomplished, but it is now found that the reaction will take place in aqueous solution.

A cooled solution of bromine in sodium hydroxide is treated with the requisite quantity of the diamide, and the mixture warmed at 60—70°, the isolation of the required base being subsequently effected by known methods. F. M. G. M.

White Precipitate. M. ZIPKIN (*Chem. Zentr.*, 1909, ii, 1914—1915; from *Apoth. Zeit.*, 1909, **24**, 661—662).—On acting with ethyl iodide on infusible white precipitate, NH_2HgCl, for four months, *tetraethylammonium mercuri-iodide*, $2NEt_4I,3HgI_2$, is obtained as yellow crystals, m. p. 158°. On heating the components on the water-bath for six hours, either alone or in the presence of alcohol, the main product consists of ammonium mercuri-iodide, NH_2I,HgI_2, admixed with small quantities of the corresponding ethylamine compound and a little ammonium chloride. On heating the fusible compound,

$$Hg(NH_3)_2Cl_2,$$

for six hours with methyl iodide, with or without addition of methyl alcohol, *tetramethylammonium mercuri-iodide*, NMe_4I,HgI_2, is obtained, which crystallises from boiling methyl alcohol in yellow leaflets, m. p. 241—242°. The mother liquor yields a considerable quantity of pale yellow needles, which in composition and properties resemble the product obtained previously from the infusible precipitate. On heating oxydimercuriammonium chloride, NH_2HgCl,HgO, for eight hours with methyl iodide on the water-bath and boiling with methyl alcohol, lemon-yellow, leaf-like crystals, m. p. 187—188°, are obtained, which behave like tetramethylammonium mercuri-iodide.

Sodium thiosulphate at the ordinary temperature expels the nitrogen from the two white precipitates, and also from the oxy-compound, almost completely as ammonia; the ammonia-free solution has a strongly alkaline reaction, and probably contains a complex of mercuric and sodium thiosulphates.

The author thinks the following formulæ are more appropriate than the accepted ones. Infusible precipitate, NHg_2Cl,NH_4Cl; fusible precipitate, $NHg_2Cl,3NH_4Cl$, and the oxy-compound, NHg_2Cl,H_2O. L. DE K.

Natural Occurrence of *d*-Asparagine. HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 89—95).—The naturally-occurring

α-amino-acids are all optically active; hitherto, only one of the two isomeric forms has been found in each case. A seeming exception to this is afforded by *d*-asparagine, isolated by Piutti (*Gazzetta*, 1887, **17**, 182) in small quantity, together with a large proportion of *l*-asparagine, from a very considerable quantity of vetch seedlings. Doubt is cast, however, on this observation by the fact that asparagine is relatively easily racemised on boiling with water; the relative greater solubility of *d*-asparagine makes it easy to separate this isomeride. Probably the *d*-asparagine described by Piutti was formed from *l*-asparagine and does not occur naturally. E. F. A.

Compounds of Amino-acids and Ammonia. IV. PETER BERGELL and HANNS VON WÜLFING (*Zeitsch. physiol. Chem.*, 1910, **64**, 348—366. Compare Fischer and Königs, Abstr., 1905, i, 31; Königs and Mylo, *ibid.*, 1909, i, 87).—Attempts have been made to prepare the amides of amino-acids by the action of ammonia on the chlorinated acyl-amides. A fairly good yield of glycinamide hydrochloride (m. p. 186—189°) is obtained by the action of aqueous ammonia on chloroacetamide at 0° and subsequent precipitation with alcohol. *dl*-Alaninamide hydrobromide can be obtained directly by vigorously stirring ethyl bromopropionate with 25% aqueous ammonia at 6° and evaporation under reduced pressure at 45°. It crystallises from absolute alcohol, has m. p. 176—177° (corr.), and yields a naphthalenesulphonyl derivative, m. p. 218°.

A good yield of *dl*-aminobutyramide hydrobromide is obtained by shaking ethyl α-bromobutyrate with 25% aqueous ammonia at 0° and evaporating the resulting solution under reduced pressure. It has m. p. 185—188° (corr.). The amide of α-bromo*iso*valeric acid does not react to an appreciable extent with ammonia, even when heated for three hours at 100°.

*Bromo*iso*hexoamide*, $CHMe_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO{\cdot}NH_2$, obtained by pouring the bromide into aqueous ammonia at 0°, crystallises in slender needles, m. p. 95—97° (corr.), and when heated with alcoholic ammonia at 100° for five hours yields leucinamide hydrobromide (68% yield), which forms long, hard prisms, m. p. 205° (corr.).

Naphthalenesulphonylglycinamide, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, has m. p. 176—178° (corr.); benzoylglycinamide has m. p. 183—185° (corr.), and *chloroacetylglycinamide*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, obtained by the action of an ethereal solution of chloroacetyl chloride on free glycinamide, crystallises in pointed plates, m. p. 130—132° (corr.).

Leucinamide is hydrolysed by trypsin, the *l*-compound being decomposed more readily than the *d*-isomeride. Glycinamide and alaninamide are not hydrolysed by trypsin, and natural asparagine is not decomposed by pancreatin. J. J. S.

Synthesis of Polypeptides. Derivatives of *iso*Leucine. II. EMIL ABDERHALDEN and JOSEF SCHULER (*Ber.*, 1910, **43**, 907—913. Compare Abstr., 1909, i, 769).—The preparation of *glycyl*-l-iso*leucine*, l-*leucyl*-l-iso*leucine*, and l-*leucyl-glycyl*-d-iso*leucine* is described. Glycyl-l-*iso*leucine is not hydrolysed by pressed yeast juice; it behaves in this

respect similarly to other polypeptides containing the antipodes of the natural amino-acids.

Chloroacetyl-l-iso*leucine*, $CH_2Cl\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, softens at 74°, m. p. 81°, $[\alpha]_D^{20}$ $-22\cdot03°$ ($\pm0\cdot2°$). *Glycyl*-l-iso*leucine*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, crystallises in long, rectangular prisms with constricted ends, which sinter at 245° (corr.), m. p. 257° (corr.) to a brown liquid. Glycyl-*d*-*iso*leucine (compare Abstr., 1909, i, 770) is now found to sinter at 246° (corr.), m. p. 256° (corr.). Glycyl-*l*-*iso*leucine has $[\alpha]_D^{20}$ $+13\cdot14°$, the *d*-isomeride having $[\alpha]_D^{20}$ $-14\cdot7°$.

Glycyl-l-iso*leucine anhydride*, $CH_2{<}{}^{NH\cdot CO}_{CO\cdot NH}{>}CH\cdot CHMeEt$, closely resembles the antipode, crystallising in spherical aggregates of needles, m. p. 262° (corr., decomp.), $[\alpha]_D^{20}$ $-17\cdot48°$ ($\pm0\cdot3°$). *d*-α-*Bromo*iso*hexoyl*-l-iso*leucine*, $CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt$, crystallises in colourless, microscopic octahedra, which sinter at 104° (corr.), m. p. 113° (corr.), $[\alpha]_D^{20}$ $+18\cdot95°$ ($\pm0\cdot6°$).

l *Leucyl*-l-iso*leucine*, prepared by the action of 25% aqueous ammonia on the bromo-compound, crystallises with $1\frac{1}{2}H_2O$ in well-formed, long needles and plates. It sinters at 278° (corr.), m. p. 283·5° (corr.), $[\alpha]_D^{20}$ $+53\cdot11°$ ($\pm0\cdot3°$).

d-α-*Bromo*iso*hexoyl-glycyl*-d-iso*leucine*, prepared from glycyl-*d*-*iso*leucine, *d*-α-bromo-*d*-*iso*hexoyl chloride, and sodium hydroxide, crystallises in well-formed plates, which sinter at 138°, m. p. 147°, $[\alpha]_D^{20}$ $+37\cdot3°$ ($\pm0\cdot5°$).

l-*Leucylglycyl*-d-iso*leucine*,

$$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CHMeEt,$$

is amorphous; it becomes brown on heating at 215°, sinters at 226° (corr.), m. p. 229—230° (corr., decomp.), $[\alpha]_D^{20}$ $+14\cdot97°$ ($\pm0\cdot2°$). It shows a marked biuret reaction. E. F. A.

ε-Amino-α-guanidinohexoic Acid. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1910, **43**, 934—936).—ε-Benzoylamino-α-bromohexoic acid reacts with a concentrated aqueous solution of guanidine, forming *ε-benzoylamino-α-guanidinohexoic acid*,

$$C_6H_5\cdot CO\cdot NH\cdot[CH_2]_4\cdot CH(CO_2H)\cdot NH\cdot C(:NH)\cdot NH_2,$$

crystallising in colourless needles, m. p. 236—241° (corr., decomp.). On boiling this with hydrochloric acid, the benzoyl group is eliminated and a *hydrochloride*, $C_7H_{14}ON_4,2HCl$, is formed; this is regarded as *ε-amino-α-guanidinohexoic anhydride dihydrochloride*,

$$HCl,NH_2\cdot[CH_2]_4\cdot CH{<}\begin{matrix}CO-NH,HCl\\ \quad\ \ |\\ NH\cdot C:NH\end{matrix}.$$

It crystallises in microscopic prisms, m. p. 212° (corr.). The *picrate* forms microscopic, yellow crystals, mostly obliquely cut prisms or plates, m. p. 225—230° (corr., decomp.). The corresponding base has not yet been isolated, and is still under investigation.

α-Bromo-δ-nitrobenzoylaminovaleric acid reacts in the same manner with guanidine. E. F. A.

Aliphatic Nitro-compounds. VII. Influence of Negative Atoms and Groups in Derivatives of Acetonitrile and Acetamide. WILHELM STEINKOPF [with LUDWIG BOHRMANN,

H. Grünupp, G. Kirchhoff, Boris Jürgens, and C. Benedek] (*J. pr. chem.*, 1910, [ii], 81, 97—149, 193—253).—After pointing out the importance of nitroacetonitrile in connexion with the constitution of fulminic acid, the author details the history of many investigators' unsuccessful attempts to synthesise the nitrile. The author hoped that the reaction between dichloroacetonitrile and hydroxylamine would yield oximinoacetonitrile, which could then be oxidised to nitroacetonitrile. The reaction results, however, in the formation of *dichloroethenylamidoxime*, $CHCl_2 \cdot C(NH_2):NOH$, m. p. 103—104° (decomp.) [*hydrochloride*, m. p. 135° (decomp.); *acetyl* derivative, m. p. 114—115°], and with an excess of hydroxylamine at 60° in the production of *oximinoethenylamidoxime*,

$$NOH:CH \cdot C(NH_2):NOH,$$

m. p. 148—152° (decomp.), the *diacetyl* derivative of which has m. p. 142—150°. In a similar way, by the interaction of the nitrile, hydroxylamine hydrochloride, and sodium carbonate in aqueous solution, a whole series of α-halogenated amidoximes can be prepared, which yield hydrochlorides with hydrogen chloride, acetyl derivatives with cold acetic anhydride, characteristic colour reactions with ferric chloride, and coloured precipitates with copper salts. *Chloroethenylamidoxime*, $CH_2Cl \cdot C(NH_2):NOH$, m. p. 91—92° (decomp.) [*hydrochloride*, m. p. 116—118° (decomp.)], *trichloroethenylamidoxime*, $CCl_3 \cdot C(NH_2):NOH$, m. p. 128—129° (decomp.) [*hydrochloride*, m. p. 140° (decomp.)], *chloro-oximinoethenylamidoxime*, $NOH:CCl \cdot O(NH_2):NOH$, decomposing at 109°, *bromoethenylamidoxime*, $CH_2Br \cdot C(NH_2):NOH$, m. p. 95—96°, *dibromoethenylamidoxime*, $CHBr_2 \cdot C(NH_2):NOH$, m. p. 120° [*hydrochloride*, m. p. 163—165° (decomp.)], *tribromoethenylamidoxime*, $CBr_3 \cdot C(NH_2):NOH$, m. p. 126°, and *iodoethenylamidoxime*, $CH_2I \cdot C(NH_2):NOH$, m. p. 123—124° (decomp.) (*acetyl* derivative, m. p. 103—105°), have thus been obtained. They are all characterised by their stability towards boiling water, hydroxylamine being produced only by heating with water under pressure. *Trichloroacetimino-methyl ether*, $CCl_3 \cdot C(:NH) \cdot OMe$, b. p. 148—149°, obtained by boiling a methyl-alcoholic solution of trichloroacetonitrile, is the first recorded instance of the formation of an imino-ether without the presence of hydrogen chloride; by heating it with aniline on the water-bath, *trichloroacetophenylamidine*, $CCl_3 \cdot C(:NH) \cdot NHPh$, m. p. 101°, is obtained, the *hydrochloride* of which has m. p. 183°.

The author's next attempt to prepare nitroacetonitrile has been more successful. According to Meister, methazonic acid is very probably β-nitroacetaldoxime, the presence of the C·C linking being indicated by the author's discovery that the interaction of methazonic acid and aqueous potassium hydroxide is a very good method of obtaining potassium nitroacetate. If the aldoxime has the *syn*-configuration, dehydration should result in the formation of nitroacetonitrile. This is the case, the nitroacetonitrile obtained by the slow addition of thionyl chloride to a boiling ethereal solution of methazonic acid being purified through the red *ammonium* salt, which decomposes at 130—135°. The presence of the primary nitro-group is proved by Konowaloff's colour reaction with ferric chloride, by the formation of *cyanomethylnitrolic acid*, $CN \cdot C(NO_2):NOH$, with nitrous acid, and by the

formation from ammonium *aci*-nitroacetonitrile and benzenediazonium nitrate of *nitrocyanoformaldehydephenylhydrazone*, $CN\cdot C(NO_2):N\cdot NHPh$, decomposing at 108°, which dyes wool intensely yellow. The presence of the cyano-group is shown by the formation of *nitroethenylamidoxime*, $NO_2\cdot CH_2\cdot C(NH_2):NOH$, decomposing at 108°, from concentrated aqueous hydroxylamine hydrochloride and ammonium *aci*-nitroacetonitrile. Nitroacetonitrile cannot be directly hydrolysed to nitroacetamide, which is produced, however, by passing hydrogen chloride into an ethereal solution of the nitrile and methyl alcohol in a freezing mixture, probably by the decomposition of the initially formed $NO_2\cdot CH_2\cdot C(OMe):NH,HCl$. Concentrated aqueous ammonium *aci*-nitroacetonitrile yields *dichloronitroacetonitrile*, $NO_2\cdot CCl_2\cdot CN$, b. p. 39°/21 mm., and *dibromonitroacetonitrile*, b. p. 57—58°/12 mm., with chlorine and bromine respectively. An ethereal solution of nitroacetonitrile at 0° reacts with amines to form the *amidines*: $C_8H_9O_2N_3$, m. p. 80°, from aniline; $C_9H_{11}O_2N_3$, m. p. 77—78°, from *o*-toluidine; $C_{10}H_{13}O_2N_3$, m. p. 86—86·5°, from *m*-xylidine.

Dipotassium nitroacetate, $CO_2K\cdot CH:NO\cdot OK$, is also produced by boiling concentrated aqueous potassium hydroxide with ammonium fulminate, ammonium *aci*-nitroacetonitrile, ammonium *aci*-nitroacetamide, or nitromethane; it forms colourless crystals, yields nitromethane with dilute sulphuric acid, and nitroacetic acid by treating its suspension in dry ether with hydrogen chloride.

β-Oximino-oxalimino-chloride, $NOH:C(OH)\cdot CCl:NH$, m. p. 157—158°, is obtained by the slow addition of ammonium nitroacetamide to an excess of thionyl chloride, and heating at 50—60°; by the addition of thionyl chloride to ethereal methazonic acid, best in sunlight; and by passing hydrogen chloride into an ethereal suspension of nitroacetamide at 0°, or into an ethereal solution of nitroacetonitrile. The *acetyl* derivative, $OH\cdot C(:NOAc)\cdot CCl:NH$, has m. p. 131°; the *benzoyl* derivative has m. p. 169°; *β-oximino-oxalphenylamidine*, $NOH:C(OH)\cdot C(:NH)\cdot NHPh$, m. p. 185°, is obtained by boiling an aqueous solution of the imido-chloride with aniline, and *β-oximino-hydroxamic acid*, $NOH:C(OH)\cdot CO\cdot NH_2$, m. p. 137°, by boiling the concentrated aqueous solution alone. *α-Oximino-oxalimino-chloride*, $NOH:C(OH)\cdot CCl:NH$, m. p. 173—174° (decomp.), obtained by saturating a boiling ethereal solution of methazonic acid with hydrogen chloride, forms an *acetyl* derivative, m. p. 165°, and a *phenylamidine*, $NOH:C(OH)\cdot C(:NH)\cdot NHPh$, m. p. 136—137°. From methazonic acid two *substances*, $C_4H_4O_4N_4$, have been obtained, the constitutions of which have not yet been ascertained; they are called α- and β-methazonic anhydrides. *α-Methazonic anhydride*, m. p. 168°, is produced by the addition of dry methazonic acid to concentrated sulphuric acid at 30—40°. It is easily soluble in dilute alkalis and in ammonium hydroxide; the yellow *sodium* and the white *silver* derivatives of the anhydride are described. The *dibenzoyl* derivative has m. p. 184—185°. An aqueous solution of the sodium derivative and diazobenzene chloride yield the *phenylhydrazone*,

$$C_4H_2O_4N_4,N_2HPh,$$

of the anhydride. By boiling a concentrated aqueous solution of α-methazonic anhydride with aniline hydrochloride, a *substance*,

$C_4H_3O_3N_4Ph$, m. p. 122°, is obtained, which forms yellow crystals; analogous coloured *substances* are obtained from the hydrochlorides of *o*- and *p*-toluidine, *p*- and *m*-phenylenediamine, and anthranilic acid, which decompose at 178—179°, 141°, 220°, 216°, and 226° respectively. *β-Methazonic anhydride*, m. p. 121—122°, is prepared by boiling the α-anhydride with water for seven minutes, recrystallising rapidly from water, and finally precipitating the solution in dilute sodium hydroxide with dilute hydrochloric acid. When the α-anhydride is boiled with water, an *oil*, $C_3H_3O_3N_3$, is formed, which yields a *phenylhydrazone*, m. p. 131°, identical with that obtained from an ammoniacal solution of β-methazonic anhydride and benzenediazonium chloride.

The following substances are obtained by heating equal molecular quantities of a halogenated acetamide and phosphorus pentachloride and exposing the initial, usually oily, product to moist air; *dichloroacetamidophosphoryl dichloride*, $CHCl_2\cdot CO\cdot NH\cdot POCl_2$, m. p. 112—113°, *diethyl* ester, $CHCl_2\cdot CO\cdot NH\cdot PO(OEt)_2$, m. p. 72—73°, *dianilide*, m. p. 219—220°, *bisphenylhydrazide*, m. p. 190° (decomp.); *trichloroacetamidophosphoryl dichloride*, m. p. 146—148°, *dimethyl* ester, m. p. 105—107°, *diethyl* ester, m. p. 47—48°, *dianilide*, m. p. 194—195°, *bisphenylhydrazide*, m. p. 237—238° (decomp.); *tribromoacetamidophosphoryl dichloride*, m. p. 105—106°, which with alcoholic sodium ethoxide gives *diethyl dibromoethoxyacetamidophosphate*, m. p. 91°; the corresponding *methyl* compound has m. p. 92—93°; *diethyl chlorobromoacetamidophosphate* has m. p. 67—68; *dichlorobromoacetamidophosphoryl dichloride*, m. p. 147°, *dimethyl* ester, m. p. 107°, *diethyl* ester, m. p. 76—77°; *dichloronitroacetamidophosphoryl dichloride*, m. p. 165° (decomp.), *diethyl* ester, m. p. 56°; *dibromonitroacetamidophosphoryl dichloride*, m. p. 187—188° (decomp.); *chlorodiphenylacetamidophosphoryl dichloride*, m. p. 122—123°, *dimethyl* ester, m. p. 104—106°; *α-dichloropropionamidophosphoryl dichloride*, $CCl_2Me\cdot CO\cdot NH\cdot POCl_2$, m. p. 127—128°.

The results of the preceding experiments show that negative atoms or groups may exert an inhibiting or a furthering influence on other portions of the molecule of an organic compound. The furthering influence is illustrated by the formation of dichloro- and dibromonitroacetonitrile from nitroacetonitrile, whilst nitromethane yields only bromonitromethane, also by the increased ability of the nitrile group to form additive compounds, not only in nitroacetonitrile, but also in the halogenated nitriles, as, for example, in the unique formation of trichloroacetimido-methyl ether. The inhibiting influence of the negative atoms or groups is shown in the difficulty of hydrolysing nitrophenylacetonitrile or nitroacetonitrile, and the stability of the nitrated and halogenated amidoximes, and especially of β-oximinooxalimido-chloride, towards water. At present there is insufficient evidence for the formulation of general rules regarding the inhibiting and the furthering influence of negative atoms or groups. C. S.

Origin of the Introduction of Magnesium into Organic Syntheses. Philippe Barbier (*Bull. Soc. chim.*, 1910, [iv], 7, 206—208).—The use of magnesium in organic syntheses is not entirely due to Grignard, since it was first employed by the author in the

preparation of dimethylheptenol by the Saytzeff reaction (Abstr., 1899, i, 323). W. O. W.

Pyrogenetic Decomposition of Naphtha in Presence of a Catalyst. IWAN VON OSTROMISSLENSKY and I. BURSCHANADZE (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 195—207).—The authors regard the formation of aromatic hydrocarbons from naphtha at high temperatures as taking place in two stages, the first being the formation of acetylene and its homologues, and the second being expressed by the reversible equation: $3C_2H_2 \rightleftharpoons C_6H_6$. It is, indeed, found that the proportion of benzene formed from naphtha is considerably increased by the presence of those contact substances, for instance, iron gauze, which facilitate the polymerisation of acetylene into benzene and polycyclic hydrocarbons. In presence of reduced nickel or its oxide, neither naphtha nor benzene yields any liquid product, the proportion of coke formed being largely increased.

Under the influence of iron or ferric oxide, asbestos, pumice, etc., at 600—750°, the hydrocarbons of the aliphatic or aromatic series or mixtures of them, such as naphtha or coal gas, are decomposed to a very considerable extent into carbon and hydrogen. The gas thus obtained may be used for filling balloons, or for heating or lighting purposes. T. H. P.

Freezing Mixtures of Isomeric Xylenes, Nitrotoluenes, and Toluidines. HERMANN W. FISCHER (*Zeitsch. Elektrochem.*, 1910, **16**, 161).—Commercial nitrotoluene (38% *p*-, 60% *o*-, and 2% *m*-nitrotoluene) deposits pure *p*-nitrotoluene on cooling; the eutectic point is reached at $-18°$. A mixture of the toluidines behaves similarly, but no eutectic point could be reached, even at $-50°$, and it is very difficult to separate the *p*-toluidine from the viscous mother liquor. *o*- and *m*-Toluidines probably solidify to amorphous glasses at very low temperatures. By freezing a mixture of the xylenes in liquid air and allowing the solid to melt slowly under suction, a solid residue melting at $+5°$ (probably nearly pure *p*-xylene) was obtained; *o*-xylene solidified about $-25°$, and *m*-xylene about $-50°$.

Apparently the molecules of these isomerides are not sufficiently similar to make them mutually soluble in the solid state. T. E.

Identity of the Solid Distyrene, m. p. 124°, with Stilbene. EMIL ERLENMEYER (*Annalen*, 1910, **372**, 247—249).—The substance formed by the dry distillation of calcium cinnamate (Engler and Leist, Abstr., 1873, 901) or β-truxillic acid (Liebermann, Abstr., 1889, 1194), and known as solid distyrene, is shown to be stilbene (compare Stobbe and Posnjak, this vol., i, 235).

Ethyl cinnamate decomposes when heated for several hours, yielding stilbene, the formation of which may be explained on the assumption that two molecules of the ester polymerise, yielding ethyl truxillate, which decomposes subsequently, partly into ethyl cinnamate and partly into stilbene and ethyl maleate. W. H. G.

Liquid and Sold Distyrene. HANS STOBBE (*Annalen*, 1910, **372**, 249—251. Compare Stobbe and Posnjak, this vol., i, 235).—The author confirms Erlenmeyer's observation (compare preceding abstract).

W. H. G.

Aniline Arsenyl Tartrate. PAUL YVON (*Compt. rend.*, 1910, **150**, 834—835. Compare this vol., i, 163) —*Aniline arsenyl tartrate*, $C_4H_5O_6(AsO)\cdot C_6H_7N$, prepared by boiling aniline hydrogen tartrate in aqueous solution with arsenious oxide, crystallises in large, hexagonal tablets, isomorphous with the corresponding antimony salt. At 100°, water is lost, with formation of an anilide. The rotatory power of an aqueous solution diminishes considerably with dilution, probably owing to dissociation; a 2% solution shows $[\alpha]_D$ 24·12°, whilst a 10% solution has $[\alpha]_D$ 58·50°. The substance has D 1·808; 100 grams of water at 15° dissolve 41·84 grams of the salt, and 756·00 grams at 100°; at 18°, 100 grams of alcohol (90%) dissolve 2·21 grams.

W. O. W.

Amines. II. Syntheses of *p*-Nitrophenylethylamine and 2:4-Dinitrophenylethylamine. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1910, **43**, 310—322).—In continuation of the authors' work on the β-amines (Abstr., 1909, i, 784), a study has been made of the nitro-derivatives of phenylethylamine.

Acetophenylethylamide (Bischler and Napieralski, Abstr., 1893, i, 608) can be obtained in a yield of 98% of the theoretical by the action of thioacetic acid on phenylethylamine, and when treated with concentrated nitric acid is converted into a mixture of *o*- and *p*-acetonitrophenylethylamide. The p-*nitro*-compound,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHAc,$$

m. p. 141—142°, is obtained in a yield of about 70% of the theoretical; it forms colourless, prismatic crystals, and is oxidised by potassium dichromate with production of *p*-nitrobenzoic acid; its *hydrochloride* has m. p. 179—180° (decomp.). The o-*nitro*-compound, m. p. 86—88°, crystallises in slender prisms, and is hydrolysed by hydrobromic acid with formation of o-*nitrophenylethylamine*, which gives a crystalline *picrate*, m. p. 147°.

p-*Aminophenylethylamine*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$, is obtained as an oil by reducing aceto-*p*-nitrophenylethylamide with tin and hydrochloric acid; the *hydrochloride* decomposes at 270—280°; the *platinichloride* has not a definite m. p., and the *picrate* has m. p. 223—224° (decomp.). *Aceto*-p-*aminophenylethylamide*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NHAc,$$

obtained by the reduction of the corresponding nitro-derivative with aluminium amalgam, crystallises in radiating prisms, sinters above 170°, and decomposes at 191—192°.

Aceto-2 : 4-*dinitrophenylethylamide*, $C_6H_3(NO_2)_2\cdot CH_2\cdot CH_2\cdot NHAc$, m. p. 97—98°, obtained by the action of a mixture of sulphuric and nitric acids on acetophenylethylamide or its *p*-nitro-derivative, crystallises in prisms, and on oxidation with potassium dichromate yields 2 : 4-dinitrobenzoic acid.

Phthalylphenylethylimide, $CH_2Ph\cdot CH_2\cdot N<{CO \atop CO}>C_6H_4$, m. p. 133°, prepared by heating phenylethylamine with phthalic anhydride, forms well-defined prisms, and, when treated with concentrated nitric acid, is converted into *phthalyl*-2 : 4-*dinitrophenylethylimide*, m. p. 215°, which crystallises in colourless, rhombic prisms.

p-*Nitrophenylethylamine*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH_2$, is obtained as a yellow oil by the hydrolysis of aceto-*p*-nitrophenylethylamide with hydrobromic or hydrochloric acid; it is a strong base, and absorbs carbon dioxide from the air to form a crystalline *carbonate*. The *hydrobromide*, m. p. 218—219°, the *hydrochloride*, m. p. 212—214°, and the *platinichloride*, which decomposes at 223°, are described. The amine reacts with phenylthiocarbimide to form *α-phenyl-β-*p-*nitrophenylethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$, m. p. 136°, which crystallises in stout prisms. *Benzenesulphonyl*-p-*nitrophenylethylamide*, $PhSO_2\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$, m. p. 107—108°, crystallises in prisms; the *methyl* derivative, $PhSO_2\cdot NMe\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2$, m. p. 98°, forms rectangular crystals.

2 : 4-*Dinitrophenylethylamine*, $C_6H_3(NO_2)_2\cdot CH_2\cdot CH_2\cdot NH_2$, obtained as an oil by the hydrolysis of aceto-2 : 4-dinitrophenylethylamide or the corresponding phthalimide with hydrochloric acid, yields a crystalline *hydrochloride*, m. p. 197—198°, and *picrate*, m. p. 159°. *α-Phenyl-β-*2 : 4-*dinitrophenylethylthiocarbamide*,

$$NHPh\cdot CS\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_4(NO_2)_2,$$

m. p. 128°, crystallises in plates. E. G.

Reaction of Imino-chlorides with Salts of Organic Acids and with Potassium Cyanide. OTTO MUMM [and, in part, HUGO HESSE] (*Ber.*, 1910, **43**, 886—893).—When a solution of *α*-chlorophenylbenzylideneamine or of *α*-chloro-*p*-nitrophenylbenzylideneamine in ether or petroleum is shaken for twenty-four hours with an aqueous solution of a salt of an organic acid, a reaction occurs which may be represented thus: $NPh{:}CPhCl + CH_3\cdot CO_2Na =$

$$NaCl + NPh{:}CPh\cdot OAc \longrightarrow NPhAc\cdot COPh.$$

In this way formylbenzanilide, acetylbenzanilide, and dibenzoylaniline have been obtained from *α*-chlorophenylbenzylideneamine and sodium formate, acetate and benzoate respectively, whilst sodium glycollate yields *hydroxyacetylbenzanilide*, m. p. 151°, and sodium cinnamate gives *cinnamoylbenzanilide*, m. p. 136°. In a similar way, *formylbenz*-p-*nitroanilide*, m. p. 165°, *acetylbenz*-p-*nitroanilide*, m. p. 180°, and *dibenzoyl*-p-*nitroaniline*, m. p. 203°, are obtained from *α*-chloro-*p*-nitrophenylbenzylideneamine.

The first stage of the preceding reaction also proceeds during the interaction of imino-chlorides and potassium cyanide; thus benzanilide and *α*-chloro-*p*-nitrophenylbenzylideneamine yield phenyliminobenzoyl cyanide (Sachs, Abstr., 1901, i, 272) and *p*-nitrophenyliminobenzoyl cyanide respectively. C. S.

Action of Acetone on Sodium Phenyl Carbonate. J. MOLL VAN CHARANTE and P. J. MONTAGNE (*Chem. Weekblad*, 1910, **7**, 166—167. Compare Moll van Charante, Abstr., 1908, i, 175; Franchimont, Abstr., 1909, i, 4).—Franchimont's statement that the

interaction of sodium phenyl carbonate and acetone dried over phosphoric oxide does not yield a vigorous evolution of carbon dioxide is admitted by him to be incorrect. A. J. W.

Preparation of Halogen and Amino-derivatives of Aromatic Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 216642).—Products obtained by the interaction of diazotised *peri*-aminonaphtholsulphonic acids with aminophenyl ethers have previously been described; the halogen derivatives of these ethers are now found to give satisfactory results, and the following are described in the patent.

p-*Chloro*-o-*aminophenyl ether*, $C_6H_5\cdot O\cdot C_6H_3Cl\cdot NH_2$, m. p. 45°, colourless prisms.

p-*Chloro*-o-*aminophenyl* m-*tolyl ether*, $C_6H_4Me\cdot O\cdot C_6H_3Cl\cdot NH_2$, m. p. 43·5°, b. p. 210°/17 mm.; warm concentrated sulphuric acid yields a *sulphonic acid*.

p-*Chloro*-o-*aminophenyl* p-*tolyl ether*, colourless needles, m. p. 55·5°; the *hydrochloride* is sparingly soluble, and dissociates with water. Concentrated sulphuric acid gives a sparingly soluble *sulphonic acid*.

2-*Chloro*-2'-*aminophenyl ether*, $NH_2\cdot C_6H_4\cdot O\cdot C_6H_4Cl$, yellow oil, decomposes when distilled under atmospheric pressure, b. p. 197°/23 mm.; the *sulphonic acid* is readily soluble in water.

4-*Chloro*-2'-*aminophenyl ether* is a yellow oil, b. p. 208°/26 mm.; the *sulphonic acid* is sparingly soluble in water.

4 : 2'-*Dichloro*-2-*aminophenyl ether*, $NH_2\cdot C_6H_3Cl\cdot O\cdot C_6H_4Cl$, is a viscous oil, b. p. 219°/20 mm.; the *sulphonic acid* is described.

4 : 4'-*Dichloro*-2-*aminophenyl ether*, colourless needles, m. p. 65°, is readily soluble in organic solvents; the *hydrochloride* (long, colourless needles) is sparingly soluble; sulphuric acid (20% anhydride) at 100° yields a *product* of high melting point which is insoluble in water, ammonium hydroxide, or sodium carbonate.

2-*Chloro*-4'-*aminophenyl ether*, $NH_2\cdot C_6H_4\cdot O\cdot C_6H_4Cl$, m. p. 82·5°, is sparingly soluble in alcohol; the sulphonated product is not readily soluble in water.

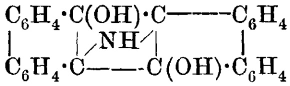
4-*Chloro*-4'-*aminophenyl ether* forms yellow prisms, m. p. 100°; the *hydrochloride* and *sulphonic acid* are described.

2 : 4'-*Dichloro*-4-*aminophenyl ether*, $NH_2\cdot C_6H_3Cl\cdot O\cdot C_6H_4Cl$, has m. p. 74°, and darkens rapidly on exposure to air; the *sulphonic acid* is sparingly soluble; sulphuric acid (20% anhydride) yields a *compound* which is insoluble in water or alkalis.

The preparation and properties of numerous dyes prepared from these compounds combined with diazotised aminonaphtholsulphonic acids are described and tabulated in the patent. F. M. G. M.

Phenanthrene Series. XXVII. Action of Ammonia and Amines on 9-Hydroxyphenanthrene, 9 : 10-Dihydroxyphenanthrene (Hydrophenanthraquinone), and 3-Bromo-9(10)-hydroxyphenanthrene. JULIUS SCHMIDT and HERMANN LUMPP (*Ber.*, 1910, **43**, 787—794).—The reaction between ammonia and 9 : 10-dihydroxyphenanthrene has been studied with the object of obtaining an in-

expensive method for the preparation of the corresponding diamino-derivative; only one of the hydroxy-groups, however, is reactive, and the product is a 9-diphenanthrol-10-amine, $NH(C_{14}H_8\cdot OH)_2$, which is not identical with the product obtained by the action of ammonia on 9-chloro-10-hydroxyphenanthrene (Abstr., 1909, i, 35). It is suggested that the latter compound has the normal structure $NH(C_{14}H_8\cdot OH)_2$, but that the former compound has the annexed isomeric formula.



(I.)

9 : 10-Dihydroxyphenanthrene is readily prepared by reducing phenanthraquinone with zinc dust and glacial acetic acid. *Di-9-hydroxyphenanthryl-10-amine*, $C_{28}H_{19}O_2N$ (formula I), forms a brown powder, m. p. 385°. Its salts with mineral acids are hydrolysed by water, and its solution in sulphuric acid has a blue colour.

Boiling aniline reacts with 9 : 10-dihydroxyphenanthrene, yielding 9-*hydroxy*-10-*anilinophenanthrene*, $OH\cdot C_{14}H_8\cdot NHPh$, which crystallises in pale green prisms, m. p. 165°. Its solution in concentrated sulphuric acid has a pale yellow colour, but gives an intense red coloration with a trace of potassium nitrate.

Di-9-phenanthrylamine, $NH(C_{14}H_9)_2$, prepared by heating 9-hydroxyphenanthrene with a concentrated aqueous solution of ammonium hydroxide on the water-bath, forms a pale brown mass, m. p. 370°. Its solution in concentrated sulphuric acid has an intense blue colour, but in the presence of a trace of the original hydroxy-compound the colour changes to green.

Di-3-bromo-9(10)-phenanthrylamine, $NH(C_{14}H_8Br)_2$, obtained from 3-bromo-9(10)-hydroxyphenanthrene and aqueous ammonium hydroxide, forms brown, flocculent masses, and is a feeble base.

3-*Bromo*-9 : 10-*dihydroxyphenanthrene*, $C_{14}H_7Br(OH)_2$, obtained by reducing 3-bromophenanthraquinone with zinc dust and glacial acetic acid, forms a colourless, flocculent mass, m. p. 220°. The *acetyl* derivative, $C_{18}H_{13}O_4Br$, forms reddish-brown crystals, m. p. 176—178°.

J. J. S.

Preparation of Aminoacylcatechols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 216640).—The action of phthalimido-fatty acid chlorides on catechol ethers in the presence of aluminium chloride yields phthalimidoacylcatechol ethers, which, on treatment with acid, are converted into aminoacylcatechols.

Phthalimidoacetoveratrole, $C_6H_4{<}{CO \atop CO}{>}N\cdot CH_2\cdot CO\cdot C_6H_3(OMe)_2$, m. p. 202°, prepared from veratrole and phthalyl glycyl chloride, when heated at 150° during one hour with concentrated hydrochloric acid (15 parts) and glacial acetic acid (20 parts) yields on addition of ammonium hydroxide *aminoacetocatechol*; its *hydrochloride* forms colourless needles, m. p. about 260°; this decomposition may be effected in two stages, the phthalic acid residue being eliminated by boiling under reflux, and the methyl groups subsequently under pressure.

a-Phthalimidopropionylveratrole,

$$C_6H_4<\substack{CO\\CO}>N\cdot CHMe\cdot CO\cdot C_6H_3(OMe)_2,$$

m. p. 212°, is prepared analogously from a-phthalimidopropionyl chloride, and yields *a-aminopropionylveratrole*, a white, crystalline powder, m. p. 220°, which on further heating forms 4-*a-aminopropionylcatechol*, $NH_2\cdot CHMe\cdot CO\cdot C_6H_3(OH)_2$, a yellow powder, m. p. 212°; its *hydrochloride*, rose-coloured leaflets, m. p. 236°, is soluble in water, and gives a green colour with ferric chloride.

4-*β-Aminopropionylcatechol*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot CH_2\cdot NH_2$, a brownish-grey powder, decomposes without melting when heated; the *hydrochloride*, leaflets, m. p. 240°, gives a characteristic green coloration with ferric chloride. F. M. G. M.

Method of Formation of Dithymol. A. BRISSEMORET and BLANCHETIÈRE (*Bull. Soc. chim.*, 1910, [iv], 7, 235—236. Compare Cousin, Abstr., 1908, i, 84, 162).—The presence of a ferment is not necessary for the conversion of thymol into dithymol. This substance can be prepared by dissolving thymol (16 grams) in 300 c.c. of alcohol and 200 c.c. of hydrogen peroxide (12 volumes), and allowing the mixture to remain for three weeks in sunlight. W. O. W.

Condensation of Benzaldehyde with Guaiacol. WILHELM MANCHOT (*Ber.*, 1910, 43, 949—951).—The condensation products of aromatic aldehydes and guaiacol or creosol are generally viscous, the only exception being the crystalline substance obtained from benzaldehyde and guaiacol. A cold mixture of concentrated sulphuric acid and glacial acetic acid is added to a solution of guaiacol (2 mols.) and benzaldehyde (1 mol.) in glacial acetic acid cooled below 0°. After five hours the mixture is poured on ice; the red oil after purification is obtained in colourless crystals, m. p. 148°, which are soluble in dilute sodium hydroxide. The analytical data and the molecular weight indicate that the substance is *phenyldiguaiacylmethane*,

$$CHPh[C_6H_3(OH)\cdot OMe]_2.$$

C. S.

p-Thiocresol. THEODOR ZINCKE and W. FROHNEBERG (*Ber.*, 1910, 43, 837—848. Compare Abstr., 1909, i, 643).—Bromine and chlorine react with a glacial acetic acid solution of *p*-thiocresol, yielding the corresponding sulphonyl chloride and bromide, an intermediate product being the disulphide. This reaction appears to be characteristic of the aromatic mercaptans as a class. With carbon tetrachloride solutions at 100°, bromine yields 3 : 3′-di- or 2 : 2′ : 5 : 5′-tetra-substituted derivatives of the disulphide.

When the methyl derivative, $C_6H_4Me\cdot SMe$, reacts with chlorine in carbon tetrachloride solution, the substituted derivative,

$$C_6H_4Me\cdot SCCl_3,$$

is obtained, whereas a solution of bromine yields an additive compound, $C_6H_4Me\cdot SMeBr_2$, or substituted derivatives,

$$C_6H_3BrMe\cdot SMeBr_2$$

and $C_6H_2Br_2Me{\cdot}SMeBr_2$. The additive products readily exchange the two bromine atoms for oxygen, yielding sulphoxides; they also react with sodium hydrogen sulphite, giving up the two bromine atoms and yielding the sulphides, which can be oxidised by nitric acid or hydrogen peroxide to the sulphoxides or sulphones.

When the methyl derivative is brominated in the absence of a solvent, the methyl group is removed and a dibromo-disulphide is obtained, which, on further bromination in carbon tetrachloride solution, yields the same tetrabromo-derivative as is obtained when the thiocresol is brominated in carbon tetrachloride solution. The dibromo-disulphide obtained from the methyl derivative contains the two bromine atoms in the *o*-positions with respect to the methyl groups, as it yields a sulphonyl chloride identical with that obtained from *o*-bromotoluenesulphonic acid.

p-*Toluenesulphonyl bromide*, $C_6H_4Me{\cdot}SO_2Br$, crystallises in colourless, flat prisms, m. p. 93—94°.

3 : 3′-*Dibromo*-p-*ditolyl disulphide*, $S_2(C_6H_3BrMe)_2$, crystallises in glistening plates, m. p. 88°, and reacts with chlorine in glacial acetic acid solution, yielding 3-*bromo*-p-*toluenesulphonyl chloride*,

$C_6H_3BrMe{\cdot}SO_2Cl$,

m. p. 80°. 2 : 2′-*Dibromo*-p-*ditolyl disulphide* forms stout, colourless needles, m. p. 100°, and yields with chlorine, 2-bromo-*p*-toluene sulphonyl chloride, m. p. 60° (Hayduck, *Annalen*, 1874, **172**, 207, gives 54°).

2 : 2′ : 5 : 5′-*Tetrabromo*-p-*ditolyl disulphide*, $S_2(C_6H_2Br_2Me)_2$, crystallises in compact, colourless cubes, m. p. 169—170°.

2-*Bromo*-p-*thiocresol*, $C_6H_3BrMe{\cdot}SH$, obtained from the corresponding disulphide by reducing with potassium sulphide, forms small crystals, m. p. 40°, and is readily oxidised to the disulphide.

p-*Tolyl methyl sulphide dibromide*, $C_6H_4Me{\cdot}SMeBr_2$, obtained by the addition of bromine to Auwers and Arndt's *p*-tolyl methyl thioether (Abstr., 1909, i, 175), crystallises in yellowish-red needles, m. p. 55—60° (decomp.). The corresponding *sulphoxide*, $C_6H_4Me{\cdot}SMeO$, has b. p. 168°/38 mm. and m. p. 50—54°; it is deliquescent, yields a sparingly soluble compound with mercuric chloride, and reacts with fuming hydrobromic acid, yielding the dibromide, $C_6H_4Me{\cdot}SMeBr_2$.

2-*Bromo*-p-*tolyl methyl sulphide dibromide*, $C_6H_3MeBr{\cdot}SMeBr_2$, forms long, brownish-red needles, m. p. 90—95° (decomp.). The *sulphoxide*, $C_6H_3MeBr{\cdot}SMeO$, has b. p. 198—200°/30 mm., and the *sulphone*, $C_6H_3MeBr{\cdot}SMeO_2$, m. p. 101°.

2 : 5-*Dibromo*-p-*tolyl methyl sulphide dibromide*, $C_6H_2MeBr_2{\cdot}SMeBr_2$, crystallises in red needles, m. p. 100—105° (decomp.), and the *sulphoxide*, $C_6H_2MeBr_2{\cdot}SMeO$, forms long, slender needles, m. p. 128°.

2-*Bromo*-p-*tolyl methyl sulphide*, $C_6H_3MeBr{\cdot}SMe$, is a colourless, odourless oil, b. p. 158°/25 mm., and the corresponding 2 : 5-*dibromo*-derivative, $C_6H_2MeBr_2{\cdot}SMe$, crystallises in long, colourless needles, m. p. 86°.

p-*Tolyl trichloromethyl sulphide*, $C_6H_4Me{\cdot}S{\cdot}CCl_3$, has b. p. 150°/15 mm. and m. p. 23°. It reacts with aniline, yielding *p*-thiocresol and triphenylguanidine. 2-*Bromo*-p-*tolyl trichloromethyl sulphide*,

$C_6H_3MeBr{\cdot}S{\cdot}CCl_3$,

crystallises in well developed plates, m. p. 57°. A by-product crystallises in needles, and has m. p. 112°. J. J. S.

Reactions and Decomposition of Tetra-alkyl-ammonium Compounds. ERNST VON MEYER (*Abhandl. Math.-phys. Klasse Sächs Ges. Wiss.*, 1909, **31**, 179—192).—A detailed account of numerous experiments relating to the reactions which occur when tetra-alkyl-ammonium compounds are treated with aromatic sulphinic acids, potassium thiocyanate, benzoic acid, sodium phenoxide, and other reagents.

The general procedure was to heat equimolecular quantities together in aqueous solution with the addition of sodium hydroxide, distil to dryness, and then continue the heating at 200° on an oil-bath and finally treat the cooled product with alcohol.

The following new compounds are mentioned: p-*Tolylmethylsulphone*, $CH_3\cdot SO_2\cdot C_7H_7$, m. p. 86°; p-*tolylethylsulphone*, m. p. 57°; p-*tolylbenzylsulphone*, $CH_2Ph\cdot SO_2\cdot C_6H_4Me$, m. p. 144·5°; *phenyl benzyl ether*, $C_6H_5\cdot O\cdot CH_2Ph$, m. p. 39°, b. p. about 280°.

F. M. G. M.

Preparation of Ethers. JOSEPH ZELTNER and B. TARASSOFF (*Ber.*, 1910, **43**, 941—945).—The interaction of *s*-dichloro- or dibromo-methyl ether and organo-magnesium compounds in dry ether leads to the formation of ethers of the type $CH_2\cdot R\cdot O\cdot CH_2R'$. *iso*Amyl ether and benzyl ether have been thus prepared, and also the following new compounds: *s-Diphenylethyl ether*, $O(CH_2\cdot CH_2Ph)_2$, b. p. 194—195°/20 mm., from magnesium benzyl chloride and *s*-dichloromethyl ether. *Benzyl propyl ether*, $CH_2Ph\cdot OPr^a$, b. p. 203·5—204·5°/752 mm. (corr.), from bromobenzene, ethyl bromide, magnesium, and *s*-dichloromethyl ether. s-*Dinaphthylmethyl ether*, $(C_{10}H_7\cdot CH_2)_2O$, m. p. 117°. p-*Xylyl ether*, $(C_6H_4Me\cdot CH_2)_2O$, m. p. 61·5—62·5°, b. p. 310—311° (corr.), and the corresponding o-*xylyl* ether, b. p. 201—203°/24 mm., $D_4^{19\cdot8}$ 1·02189, $n_D^{19\cdot8}$ 1·55784, from *p*- and *o*-bromotoluene respectively. Hydriodic acid, D 1·70, converts the last two ethers almost quantitatively into iodo-*p*-xylene, m. p. 45·5—46·5°, and iodo-*o*-xylene, m. p. 34°, respectively. C. S.

1 : 2-Phenylmethylglycols [α-Phenylpropylene αβ-Glycols]. THEODOR ZINCKE and K. ZAHN (*Ber.*, 1910, **43**, 849—855. Compare Zincke, Abstr., 1884, 1003).—The dibromopropylbenzene used for the preparation of the two phenylpropylene glycols has the constitution previously ascribed to it (*loc. cit.*, 1004), as it can be obtained by the addition of bromine to propenylbenzene (Klages, Abstr., 1903, i, 329). Both glycols are formed at the same time, but the proportions depend upon the conditions of the experiment. Both are racemic compounds, but so far have not been resolved into active components. The α-glycol has m. p. 56—57°, and is best prepared by heating the dibromo-compound with potassium acetate and glacial acetic acid, and then hydrolysing the resulting acetate with alcoholic potash. When benzoylated by means of benzoic anhydride or benzoyl chloride, each glycol yields a mixture of the two benzoyl derivatives.

The *α-benzoate*, $C_{23}H_{20}O_4$, crystallises in fibrous masses, m. p. 76—77°, and the isomeric *β-compound* in small needles, m. p. 101°. When hydrolysed, each benzoate yields the corresponding glycol. The same dibromo-derivative is formed when the two glycols react with phosphorus pentabromide. When heated with dehydrating agents, both glycols yield the same pinacolin, namely, benzyl methyl ketone,

$$CH_3\cdot CO\cdot CH_2\cdot C_6H_5,$$

b. p. 214—215°. The phenylhydrazone has m. p. 86—87°, and the semicarbazone, m. p. 194—195° (compare Tiffeneau, Abstr., 1906, i, 663).

Benzaldehyde and acetaldehyde are formed when either of the two glycols is oxidised with chromic acid or permanganate. Nitric acid oxidises the glycols to the *ketonic alcohol*, COPh·CHMe·OH or

$$OH\cdot CHPh\cdot COMe,$$

which is a yellow oil, b. p. 240—242°. The *semicarbazone* crystallises in needles, and has m. p. 184—185° (decomp.), and the *benzoate*,

$$C_{16}H_{14}O_3,$$

has m. p. 109—110°. When further oxidised, the ketonic alcohol yields the diketone, COPh·COMe (compare von Pechmann and Müller, Abstr., 1888, 1087). J. J. S.

Formation of an Ethylene Oxide from the Ammonium Base of Hydroxydiphenylethylamine. PAUL RABE and JULIUS HALLENSLEBEN (*Ber.*, 1910, **43**, 884—886).—β-Hydroxy-αβ-diphenylethylamine by treatment with methyl iodide (3 mols.) and sodium methoxide (2 mols.) in methyl-alcoholic solution yields a *methiodide*,

$$OH\cdot CHPh\cdot CHPh\cdot NMe_3I,$$

m. p. 194°, from which, by means of water and silver oxide, a solution of the ammonium base is obtained; this solution yields trimethylamine and *diphenylethylene oxide*, m. p. 69°, by warming.

Erlenmeyer's stereoisomeric *iso*hydroxydiphenylethylamine (Abstr., 1899, i, 760) by similar treatment yields a *methiodide*, m. p. 219°, from the base of which a stereoisomeric iso*diphenylethylene oxide*, m. p. 42°, is obtained. The two oxides have a neutral reaction, do not give a coloration with alcoholic ferric chloride, and are unaffected by Fehling's solution, ammoniacal silver solutions, or dilute potassium permanganate. C. S.

The Cholesterol Group. VII. The Phytosterol of the Oil of the Ordinary Walnut (Juglans regia). ANGELO MENOZZI and A. MORESCHI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 187—192. Compare this vol., i, 254).—One hundred kilos. of walnuts with shells gave 38·4 kilos. of shell-free product, and this, on extraction with ether, yielded 23·2 kilos. of oil. The latter contains 0·26% of a non-saponifiable substance, which forms monoclinic crystals, m. p. 138°, $[\alpha]_D^{14}$ −33·76°, and gives the colour reactions of the members of the cholesterol group. The analytical numbers agree with the formula $C_{26}H_{43}\cdot OH$(or $C_{27}H_{45}\cdot OH$) + H_2O, and in freezing naphthalene the mol. wt. of the hydrated compound is 394. These characters correspond well with those given by Mugge (*Zeitsch. Nahr. Genussm.*, 1898, **1**, 45) for phytosterol from cotton-seed oil. The

formate, $H\cdot CO\cdot O\cdot C_{27}H_{45}$ or $H\cdot CO\cdot O\cdot C_{26}H_{43}$, forms elongated laminæ, m. p. 106°, $[\alpha]_D^{20}$ −45·0°; the acetate, prismatic needles, m. p. 121°, $[\alpha]_D^{17}$ −40·48°; the benzoate, small, orthorhombic [ARTINI: $a:b:c$ = 0·716 : 1 : 0·217] plates, m. p. 150°, $[\alpha]_D^{17}$ −14·27°, and the salicylate, crystals, m. p. 155°, $[\alpha]_D^{15}$ −50·82°, which are distinguished from all other derivatives of phytosterol by their slight solubility in alcohol (compare Golodetz, Abstr., 1908, i, 20). The acetate readily takes up Br_2, giving the *acetate* of the *dibromide*, $C_{29}H_{48}O_2Br_2$, m. p. 118°.

Dihydrophytosterol, prepared by passing hydrogen through an ethereal solution of phytosterol in presence of platinum black, has m. p. 136—137°, $[\alpha]_D^{20}$ +22·97°, and does not give the ordinary colour reaction with sulphuric acid and chloroform. Its *acetate* has m. p. 134—135°, $[\alpha]_D^{19}$ +14·27°.

Certain of the above physical data are identical with those of a phytosterol which is widespread in the vegetable kingdom.

T. H. P.

Catalysis of Aromatic Acids. JEAN B. SENDERENS (*Compt. rend.*, 1910, **150**, 702—704. Compare Abstr., 1909, i, 286, 627; this vol., i, 11, 179).—A further study of the catalytic decomposition of acids, whereby ketones are produced. The oxides of chromium, aluminium, zinc, and calcium behave towards mixtures of benzoic acid and aliphatic acids in the same way as in the case of the aliphatic acids previously examined. The dioxides of cerium, titanium, and tin are very inferior to thorium dioxide in catalytic activity. The latter substance is more rapid in its action than uranium dioxide, and more regular than zirconium oxide.

Aromatic acids, in which the carboxyl group is directly attached to a benzene or naphthalene nucleus, do not give ketones, unless mixed with an aliphatic acid, when a mixed ketone is produced. Those acids, however, in which the carboxyl group is attached to the side-chain are readily converted into the corresponding ketones; thus phenylacetic acid yields $\alpha\gamma$-diphenylacetone, whilst phenylpropionic acid furnishes $\alpha\epsilon$-diphenylpentan-γ-one.

W. O. W.

Preparation of Nitrogen Derivatives of Phenylglycine-*o*-carboxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 216748).—When derivatives of anthranilic acid of the general formula (I), where R is an aromatic residue, R′ an aryl, alkyl, or substituted $\cdot CH_2\cdot CN$ or $CH_2\cdot CO_2H$ group, react with formaldehyde, compounds of the general formula (II) are produced, which on treatment with hydrogen cyanide yield products (III), and these on hydrolysis are converted into phenylglycinecarboxylic acids (IV):

$$\underset{\text{(I.)}}{CO_2H\cdot R\cdot NHR'} \qquad \underset{\text{(II.)}}{CO\negthickspace<\negthickspace\begin{matrix} R\cdot NR' \\ | \\ O\cdot CH_2 \end{matrix}} \qquad \underset{\text{(III.)}}{CO_2H\cdot R\cdot NR'\cdot CH_2\cdot CN}$$

$$\underset{\text{(IV.)}}{CO_2H\cdot R\cdot NR'\cdot CH_2\cdot CO_2H.}$$

Anthranilodiacetic acid, $CO_2H\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, is prepared by

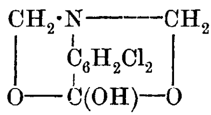
the following series of operations: ω-cyanomethylanthranilic acid is warmed at 70—80° with formaldehyde, and the resulting anhydroformaldehyde compound (m. p. 104—106°) is treated with aqueous potassium cyanide at the ordinary temperature; on addition of mineral acid, the *di-ω-cyanodimethylanthranilic acid* separates; it forms flat prisms, m. p. 168—171° (decomp.), and on alkaline hydrolysis yields the foregoing acid.

Phenylglycine-*o*-carboxylic acid on analogous treatment yields a colourless, crystalline *condensation product*, m. p. 145—148°; the *nitrile*, $CO_2H{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CO_2H){\cdot}CH_2{\cdot}CN$, is a crystalline powder, m. p. 140° (decomp.).

Diphenylglycine-o-carboxylic acid, prepared from phenylanthranilic acid, forms colourless prisms or needles, m. p. 165—167°.

These substances are employed for the production of indigotin derivatives. F. M. G. M.

Preparation of Anthranilodi-ω-acetic Acid and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 216749).—When 3 : 4-dichlorophthalic anhydride (or a mixture of isomerides) is treated with hydroxylamine, it yields 3 : 4-*dichlorophthalylhydroxylamine*, m. p. 216—219°, the more soluble 4 : 5-*dichlorophthalylhydroxylamine* remaining in solution. On hydrolysis, a mixture of 5 : 6- (chiefly) with some 3 : 4-dichloroanthranilic acid is obtained, separation being effected by boiling with dilute ammonium hydroxide and acidifying, when 3 : 4-*dichloroanthranilic acid*, m. p. 240—242°, separates from the hot liquid; on cooling, the more soluble 5 : 6-*dichloroanthranilic acid* crystallises out, m. p. 175—180°.



The inner *dianhydride* of the *methyl ether* (annexed formula), m. p. 151—152°, is prepared by treating 5 : 6-dichloroanthranilic acid (206 parts) in methyl alcoholic solution with 30% formaldehyde (250 parts); the *ethyl ether* forms needles, m. p. 123—124°.

ω-*Cyanomethylanhydroformaldehyde*-5 : 6-*dichloroanthranilic acid* [5 : 6-*dichlorodihydro*-2 : 4-*benzoxazin*-1-*one*-4-*acetonitrile*],

$$C_6H_2Cl_2{<}{\substack{N(CH_2{\cdot}CN)\\CO\text{———}O}}{>}CH_2,$$

is formed when the preceding dianhydride compound (262 parts) is treated with cold potassium cyanide (80 parts); it is insoluble in sodium carbonate, and has m. p. 169—172°; on hydrolysis it yields 3 : 4-*dichlorophenylglycine-2-carboxylic acid*, m. p. 200°.

5 : 6-*Dichloroanthranilodi-ω-acetonitrile*,

$$CO_2H{\cdot}C_6H_2Cl_2{\cdot}N(CH_2{\cdot}CN)_2,$$

is obtained by treating the corresponding mononitrile with potassium cyanide and acidifying.

5 : 6-*Dichloroanthranilodiacetic acid*, $CO_2H{\cdot}C_6H_2Cl_2{\cdot}N(CH_2{\cdot}CO_2H)_2$, needles, m. p. 190° (decomp.), is prepared by boiling the preceding dinitrile (262 parts) with sodium hydroxide (150 parts) until the ammonia is completely evolved.

The preparations of several compounds previously described are recapitulated. F. M. G. M.

Preparation of Carboxyarylsulphoxidoacetic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216725).—The arylthioglycol-*o*-carboxylic acids of the general formula

$$CO_2H{\cdot}R{\cdot}S{\cdot}CH_2{\cdot}CO_2H$$

are readily oxidised by sodium hypochlorite to the corresponding carboxyarylsulphoxidoacetic acids, $CO_2H{\cdot}R{\cdot}SO{\cdot}CH_2{\cdot}CO_2H$.

o-*Carboxyphenylsulpho-oxidoacetic acid*, $CO_2H{\cdot}C_6H_4{\cdot}SO{\cdot}CH_2{\cdot}CO_2H$, colourless crystals, m. p. 177°, is thus prepared from sodium phenylthioglycol-*o*-carboxylate. F. M. G. M.

Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Ber.*, 1910, **43**, 955—958).—The results obtained by Riiber and Goldschmidt (this vol., i, 174) do not differ materially from those described by the authors (Abstr., 1909, i, 156, 648). C. S.

Partial Hydrolysis of Proteins. EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1910, **64**, 436—446).—The authors suggest the use of β-naphthalenesulphonyl chloride for the purpose of determining the constitution of a polypeptide. The polypeptide is condensed with the chloride in the usual manner, and the resulting β-naphthalenesulphonyl derivative is subjected to hydrolysis by boiling for two to three hours with 10% hydrochloric acid and the hydrolytic products examined. The β-naphthalenesulphonyl group always remains attached to the terminal amino-acid. If a tyrosinyl group is present in the molecule of the polypeptide, then the *O*-β-naphthalenesulphonyl derivative is found among the products of hydrolysis, unless the tyrosinyl group is the terminal group of the chain of condensed amino-acids, when the disulphonyl derivative of tyrosine is obtained.

The hydrolytic products are most readily separated and isolated by Fischer's esterification method.

β-*Naphthalenesulphonyl-glycyl*-l-*tyrosine*,

$$C_{10}H_7{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}SO_2{\cdot}C_{10}H_7,$$

sinters at 90°, decomposes at 110°, and does not give a red coloration with Millon's reagent. When hydrolysed, it yields β-naphthalenesulphonylglycine and β-*naphthalenesulphonyltyrosine hydrochloride*, $C_{19}H_{18}O_5NSCl$, which sinters at 100° and melts at 170° (decomp.). The *ester hydrochloride*, $C_{21}H_{22}O_5NSCl$, sinters at 190° and has m. p. 195°.

When the β-naphthalenesulphonyl derivative of silk peptone is hydrolysed and the products are esterified, the following compounds can be isolated: β-naphthalenesulphonylalanine ethyl ester, m. p. 95° (Fischer and Bergell, Abstr., 1903, i, 24), alanine ethyl ester hydrochloride, and *O*-β-naphthalenesulphonyltyrosine ethyl ester hydrochloride.

N-β-*Naphthalenesulphonyltyrosine*,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}SO_2{\cdot}C_{10}H_7,$$

can be prepared as its *sodium* salt by the action of the sulphonyl chloride on an alcoholic solution of sodium tyrosinate. The salt sinters at 150° and decomposes at 175°. The *ethyl* ester, $C_{21}H_{21}O_5NS$, melts at 140° to a turbid liquid, which clarifies at 143°.

The di-β-naphthalenesulphonyl derivative of tyrosine is not hydrolysed when boiled with 10% hydrochloric acid. J. J. S.

[Preparation of Aldehyde Derivative of Hydroxy-aromatic Acids.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 216924).—The preparation of diphenylnaphthylmethane derivatives from hydroxynaphthaldehyde-sulphonic, -carboxylic, or -sulphonyl-carboxylic acids and salicylic acid has previously been described. It is now found that the hydroxyaldehydobenzoic acids will condense in the same manner, yielding leuco-acids, which are then oxidised with *nitrosylsulphuric acid*; the following initial compounds are mentioned in the patent: o-*aldehydo*-p-*cresotic acid*, m. p. 190°; p-*aldehydo*-o-*cresotic acid*, colourless, crystalline powder, m. p. 211°; p-*chloro*-o-*aldehydosalicylic acid*, colourless, crystalline powder, m. p. 201°; 2-*hydroxy*-5-*sulphonyl*-1-*aldehydo*-3-*benzoic acid*, colourless crystals, soluble in water. F. M. G. M.

Common Constitution of the Three Specific Biliary Acids. FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1910, **65**, 157—179).—When oxidised with a mixture of chromic and acetic acids, cholic acid forms a dehydrocholic acid, m. p. 178°, $[\alpha]_D$ +66·76°, whilst from deoxycholic acid a dehydrocholic acid, m. p. 186°, $[\alpha]_D$ + 94·4°, is obtained. When oxidised with nitric acid, both cholic acid and deoxycholic acid yield the same choloidanic acid, $C_{18}H_{28}O_8$, decomp. 324°. This was also obtained from cholalic acid; accordingly, all three biliary acids have the C_{18} residue in common. The mother liquors in each case contained a *compound*, $C_{19}H_{28}O_{10}$, m. p. 230—231°, decomp. 240°, yielding an *ethyl* ester, m. p. 195—196°, identical with diethyl ester of the pentabasic acid described by Letsche (Abstr., 1909, i, 697).

Choloidanic acid, when heated above the melting point, is converted into pyrocholoidanic acid, $C_{15}H_{20}O_4$, m. p. 217°, $[\alpha]_D$ +45·6°, which is probably ζ-p-*carboxyphenyl*-α-*methylheptoic acid*,

$$CO_2H \cdot C_6H_4 \cdot [CH_2]_5 \cdot CHMe \cdot CO_2H.$$

Constitutional formulæ are assigned to the three biliary acids. E. F. A.

Carbon Monoxide from Aldehydes. AUGUSTIN BISTRZYCKI and MARTIN FELLMANN (*Ber.*, 1910, **43**, 772—776. Compare Abstr., 1901, i, 701, 716; 1904, i, 315; 1906, i, 135; also Mundici, 1909, i, 719; Dakin, Proc., 1909, **25**, 194).—4-*Hydroxy*-3-*aldehydotriphenylacetic acid*, $CO_2H \cdot CPh_2 \cdot C_6H_3(CHO) \cdot OH$, obtained by the condensation of salicylaldehyde and benzilic acid, yields the theoretical amount of carbon monoxide when heated with sulphuric acid at 100°, and leaves 4-*hydroxy*-3-*aldehydotriphenylcarbinol*, $OH \cdot CPh_2 \cdot C_6H_3(CHO) \cdot OH$, m. p. 123—124°, which reacts with concentrated sulphuric acid at 120—190° losing carbon monoxide. Other aldehydes also react with hot sulphuric acid, the general results obtained so far indicate that whereas benzaldehyde yields but little carbon monoxide when heated with concentrated sulphuric acid, substituted benzaldehydes containing hydroxyl or methyl groups in the ortho- or para-positions evolve carbon dioxide readily. The same substituents in the meta-position do not

facilitate the evolution of carbon monoxide. *o*-Phthaldehydic acid does not yield carbon monoxide. The only aliphatic aldehyde investigated yields little carbon monoxide, but undergoes complex oxidation. J. J. S.

Preparation of Aminoaldehydes. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 217385).—The direct reduction of aromatic carboxylic acids to the corresponding aldehydes has not been recorded previously, and it is found that aminocarboxylic esters can be reduced by nascent hydrogen in either acid or neutral solution to aminoaldehydes. By this method the aldehydes of primary amines, imino-derivatives, nitriles, and tetra-alkylammonium compounds have been prepared, the reaction being general for aliphatic, aromatic, or heterocyclic compounds; the amino-group may be in the nucleus or in the side-chain, and there may be more than one acidic group present.

As reducing agents, sodium, aluminium, or calcium amalgams, magnesium powder, zinc dust, iron filings, or stannous chloride are employed.

The preparation of the aminoaldehyde from ethylglycine in aqueous solution with sodium amalgam is described, also of hydroxyphenylaminopropaldehyde with calcium amalgam, and the method is recommended for the preparation of aspartaldehyde, serinaldehyde, *iso*serinaldehyde, phenyl-α-aminopropaldehyde, α-β-diaminopropaldehyde, pyrrolidinealdehyde, and aminophenylacetaldehyde,

$$NH_2\cdot CHPh\cdot CHO.$$

F. M. G. M.

New Method for Synthesis of Unsaturated Ketones. GEORGES DARZENS (*Compt. rend.*, 1910, **150**, 707—710).—When *cyclo*hexene is treated with aluminium chloride and acetyl chloride in presence of carbon disulphide, combination occurs between the hydrocarbon and the acid chloride, and a compound is formed to which the constitution $\begin{matrix} CH_2\cdot CH_2\cdot CHCl \\ | \qquad\qquad | \\ CH_2\cdot CH_2\cdot CH\cdot COMe \end{matrix}$ is ascribed.

This forms a stable, complex compound with the aluminium chloride. On treating the product with a tertiary base, such as dimethylaniline, hydrogen chloride and tetrahydroacetophenone are produced. The latter is obtained in 50% yield if stannic chloride is substituted for aluminium chloride.

This condensation is an instance of what appears to be a perfectly general reaction, of which the Friedel and Crafts' reaction is only a particular case. The essential condition appears to be the presence of a double ethylenic linking.

The chlorides of boron, iron, and antimony may be substituted for aluminium chloride, but not with advantage. The chlorides of sulphur, silico , copper, and mercury are without action. Titanium tetrachloride gives good yields.

The author has prepared by this method a large number of new aliphatic and hydroaromatic ketones, and has extended the reaction to the condensation of alkyl halides with unsaturated hydrocarbons.

W. O. W.

Stereoisomeric Chloroimino-ketones. JULIUS STIEGLITZ and P. P. PETERSON (*Ber.*, 1910, **43**, 782—787. Compare Stieglitz and Earle, Abstr., 1904, i, 39).—The chloroimino-derivatives of unsymmetrical ketones appear to exist in two stereoisomeric modifications analogous to pairs of stereoisomeric ketoximes. This is shown in the case of the α- and β-*chloroimides* of p-*chlorobenzophenone*,

$$C_6H_4Cl\cdot CPh{:}NCl.$$

The α-compound crystallises in thin plates, m. p. 104°, and is not so soluble in a mixture of chloroform and light petroleum as the β-compound, which can be isolated as large crystals or as thin prisms and needles when its solution is cooled to −10°. It has m. p. 55°. The compounds are prepared by the action of hypochlorous acid on the corresponding benzophenoneimine; they do not undergo the Beckmann transformation, but their structural identity is shown by the fact that they both react with dry hydrogen chloride, yielding *p*-chlorobenzophenoneimide hydrochloride, which with water is decomposed into ammonium chloride and *p*-chlorobenzophenone. J. J. S.

New Isomerisation of Benzopinacolins and Le Chatelier's Law. MAURICE DELACRE (*Bull. Soc. chim.*, 1910, [iv], 7, 163—166. Compare Abstr., 1891, 456; 1902, i, 179; 1906, i, 518; 1907, i, 581, 999; 1908, i, 243; 1909, i, 807).—A discussion of the constitution of α- and β-benzopinacolin and the conditions under which these substances undergo isomerisation. W. O. W.

True Constitution of α- and β-Benzopinacolin. MAURICE DELACRE (*Bull. Soc. chim.*, 1910, [iv], 7, 167—171. Compare preceding abstract).—A critical résumé and discussion of previous work. W. O. W.

Intramolecular Atomic Transpositions. X. Influence of the Substituents of the Phenyl Group in the Transformation of α-Benzopinacolins into β-Pinacolins. P. J. MONTAGNE and S. A. KOOPAL (*Rec. trav. chim.*, 1910, [ii], **14**, 136—149. Compare Abstr., 1907, i, 854, and following abstract).—*a-s*-4 : 4′-Dichlorobenzopinacolin, $O<\begin{matrix}CPh\cdot C_6H_4Cl\\ |\\ CPh\cdot C_6H_4Cl\end{matrix}$, is converted by the action of acetyl chloride into a mixture of the two β-pinacolins: $COPh\cdot CPh(C_6H_4Cl)_2$ (40%) and $C_6H_4Cl\cdot CPh_2\cdot CO\cdot C_6H_4Cl$ (60%). In the preparation of 4-chlorobenzophenone by the Friedel and Crafts' reaction, a certain amount of 2-chlorobenzophenone is also formed.

(JAEGER.—2-Chlorobenzophenone is deposited from solutions in petrol in colourless, lustrous needles (or prisms), which are monoclinic-prismatic; $a : b : c = 0.4985 : 1 : 0.4706$; $\beta = 83°8'$.)

2-*Chlorobenzophenoneoxime* has m. p. 121°; when treated with phosphorus pentachloride it yields the anilide, $C_6H_4Cl\cdot CO\cdot NHPh$, and therefore has the constitution $\begin{matrix}C_6H_4Cl\cdot C\cdot Ph\\ \|\\ N(OH)\end{matrix}$.

a-s-4 : 4′-*Dichlorobenzopinacolin*, prepared by reducing 4-chlorobenzophenone with zinc dust, acetic acid, and sulphuric acid, has m. p.

220° (decomp.). When no sulphuric acid is added, the reduction yields chiefly the acetate of 4-chlorobenzhydrol.

4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacone is decomposed by alcoholic potassium hydroxide into 4 : 4′-dichlorobenzophenone and 4 : 4′-dichlorobenzhydrol. A blue colour appears during the reaction, and a similar colour is given by benzopinacone, *s*-4 : 4′-dichlorobenzopinacone, and *s*-4 : 4′-dibromobenzopinacone, but not by α-4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin and α-4 : 4′-dichlorobenzopinacolin. R. V. S.

Intramolecular Atomic Transpositions. XI. Influence of the Substituents of the Phenyl Group in the Transformation of Benzopinacones into Benzopinacolins. P. J. MONTAGNE (*Rec. trav. chim.*, 1910, [ii], **14**, 150—162. Compare preceding abstract).—The action of acetyl chloride on 4 : 4′-*dibromobenzopinacone*, $C_6H_4Br·CPh(OH)·CPh(OH)·C_6H_4Br$, yields a mixture of the two pinacolins: $C_6H_4Br·CPh_2·CO·C_6H_4Br$ (57—58%) and $COPh·CPh_2·C_6H_4Br$ (42—43%) (compare Abstr., 1907, i, 854). The dibromobenzopinacone is prepared by reducing *p*-bromobenzophenone with zinc dust and acetic acid; it has m. p. about 178° (decomp.). The Friedel and Crafts' reaction with *p*-bromobenzoyl chloride and bromobenzene leads to the production of some 2 : 4′-dibromobenzophenone in addition to the 4 : 4′-dibromo-compound, which is the main product. 2 : 4′-Dibromobenzophenone has m. p. 62° (Heidenreich, Abstr., 1894, i, 417, gave 51—52°) and b. p. 381—384°/764 mm.

(JAEGER.—The substance forms large, lustrous, transparent crystals, of which the symmetry is monoclinic-prismatic; $a : b \, c = 1·0962 : 1 : 0·5951$; $\beta = 68°25\frac{1}{2}'$.

4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacolin is deposited from a mixture of ethyl acetate and petrol in flat, colourless crystals of monoclinic-prismatic symmetry; $a : b : c = 1·2853 : 1 : 1·0665$; $\beta = 63°47'$.)

R. V. S.

Action of Ammonia on Tetramethyl*cyclo*butandione. EDGAR WEDEKIND and M. MILLER (*Ber.*, 1910, **43**, 834—836).—*Iminotetramethyl*cyclo*butanone*, $CMe_2<\substack{C(:NH)\\CO}>CMe_2$, is formed when tetramethyl*cyclo*butane-1 : 3-dione (Wedekind and Weisswange, Abstr., 1906, i, 437) is heated with 20% ammonium hydroxide solution at 120—130°. It crystallises in glistening, felted needles, m. p. 108·5°, dissolves readily in mineral acids, yields a *phenylhydrazone*, $C_{14}H_{19}N_3$, m. p. 162°, and is hydrolysed to the original diketone when heated with concentrated hydrochloric acid at 120—130°. J. J. S.

New Type of Quinhydrone Compound. ANGELO KNORR (*Ber.*, 1910, **43**, 798—800).—Quinone mono- and di-chloroimides form additive compounds with quinol. These resemble quinhydrone in appearance, composition, and in the readiness with which they dissociate in solution.

Quinol quinonechloroimide, $C_6H_6O_2,C_6H_4ONCl$, crystallises in blackish-green needles with a metallic lustre; it decomposes at 119°, and is resolved into its components when warmed with benzene.

Quinol quinonedichloroimide, $C_6H_6O_2,C_6H_4N_2Cl_2$, crystallises in large, blackish-green needles, which decompose at 129—130°.

Benzidine quinonedichloroimide, $2C_{12}H_{12}N_2,C_6H_4N_2Cl_2$, crystallises in deep violet-coloured needles, which decompose at 121°. J. J. S.

Preparation of Halogenated 2-Methylanthraquinone Derivatives Substituted either in the Aromatic Nucleus or in the Side-Chain. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 216715).—Bromomethylanthraquinones have been prepared previously as crystalline substances, which, on heating with alkalis at 180—200°, yielded methylalizarins identical with those prepared by the sulphonation of the corresponding methylanthraquinones and subsequent fusion with alkali.

Bromo-2-methylanthraquinone, m. p. 200—202°, is prepared by heating 2-methylanthraquinone (10 parts) with bromine (8 parts) in a sealed tube at 170° during six hours; if twice the quantity of bromine is employed, a *dibromomethylanthraquinone* is formed.

2-*Dichloromethylanthraquinone*, m. p. about 200°, is produced, along with a *monochloro*-derivative, when 2-methylanthraquinone is treated with chlorine at 150—160°. The chlorine in the foregoing reaction can be replaced by sulphuryl chloride.

When 4-bromo-1-hydroxy-2-methylanthraquinone is heated at 150—170° with half its weight of bromine during four to six hours, a *ω-bromo*-derivative is obtained, which crystallises from acetic acid in lustrous, golden needles. By analogous methods, mixed halogenated methylanthraquinones can be prepared. F. M. G. M.

Preparation of Sulphur Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 216480).—By the condensation of thiosalicylic [*o*-thiolbenzoic] acid or its derivatives with α-chloro- and α-bromo-anthraquinones, products having the following general formula are obtained:

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H = H_2O + C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{S}_{CO}{>}C_6H_4.$$

They form brown powders, which are insoluble in dilute acids, alkalis, or organic solvents, soluble in concentrated sulphuric acid, and do not melt below 350°. F. M. G. M.

A New Process for Obtaining Glycuronic Acid (and Menthylglycuronic Acid). CARL NEUBERG and S. LACHMANN (*Biochem. Zeitsch.*, 1910, **24**, 416—422).—Menthylglycuronic acid is obtained by administering menthol in the form of an emulsion (obtained by diluting an alcoholic solution with water) to a rabbit. To the acidified urine of the animal is then added one-quarter the volume of alcohol, and one-eighth of that of ether. To the ethereal extract, excess of ammonia is added, and the ammonium salt of the glycuronate separates out. Glycuronic acid can be obtained from the menthyl derivative by hydrolysis with sulphuric acid. The authors also give the preparation and composition of some basic lead salts of menthylglycuronic acid. S. B. S.

Isomeric Borneolglycuronic Acids. JUHO HÄMÄLÄINEN (*Skand. Arch. Physiol.*, 1909, **23**, 86—98).—The isomeric borneolglycuronic acids described in this paper were obtained from the urine of rabbits fed on the requisite borneol. Although Magnus-Levy has shown (Abstr., 1907, i, 228) that the animal organism is incapable of differentiating between *d*- and *l*-borneol, nevertheless the borneol resulting from the hydrolysis of the basic lead precipitate obtained from the urine of rabbits fed on *r*-borneol is distinctly lævorotatory. The borneolglycuronic acids are not acted on by emulsin, but are hydrolysed by dried yeast extract (compare, however, the following abstract); the conclusion is drawn, therefore, that these compounds are *a*-glucosides, and since they do not reduce Fehling's solution, and when hydrolysed yield the corresponding borneol and dextrorotatory glycuronic acid, probably have the constitution represented by the formula: $C_{10}H_{17}O{\cdot}CH{<}\begin{array}{l}CH(OH){\cdot}CH(OH)\\O\text{———————}CH{\cdot}CH(OH){\cdot}CO_2H\end{array}$

r-*Borneolglycuronic acid*, $C_{16}H_{26}O_7$, crystallises with $\frac{1}{2}H_2O$ in small, white needles, m. p. 94—95°; the anhydrous substance is very hygroscopic, and has m. p. 163—165°, $[a]_D^{20}$ $-47·93°$ (in water); the *zinc* salt, $C_{32}H_{50}O_{14}Zn,2H_2O$, forms long, glistening needles, and decomposes at 200° without melting.

r-iso*Borneolglycuronic acid* crystallises with $1H_2O$ in small, white needles, m. p. 104—106°; the anhydrous substance is hygroscopic, and has m. p. 162—163°, $[a]_D^{20}$ $-42·62°$ (in water); when kept for several days in a vacuum desiccator over phosphoric oxide, it partly changes into a *substance*, m. p. 205—206°, which is probably a lactone of the acid; the *zinc* salt ($2H_2O$) forms long, glistening needles, and turns black at 200°, but does not melt.

l-*Borneolglycuronic acid* is extremely hygroscopic, and has m. p. 162—163°, $[a]_D^{20}$ $-69·03°$ (in water); the hydrated acid has m. p. 96—97°; the *zinc* salt ($2H_2O$) forms glistening, white needles, and turns brown at 202° without melting; a *substance*, m. p. 206—208°, probably a lactone of the acid, was obtained as a by-product.

d-*Borneolglycuronic acid* has m. p. 164—165°, $[a]_D^{20}$ $-37·02°$; the acid crystallises with H_2O in small, white needles, m. p. 94—95°.

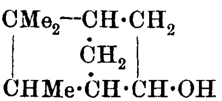
W. H. G.

Fission of Borneol- and Camphor-glycuronic Acids by Enzymes. JUHO HÄMÄLÄINEN (*Skand. Arch. Physiol.*, 1910, **23**, 297—301).—The observations recorded in the previous paper (compare preceding abstract) on the behaviour of borneolglycuronic acids towards enzymes are worthless, since the chloroform employed to render the solutions sterile contained hydrogen chloride. The borneolglycuronic acids are hydrolysed very slowly by emulsin, but not by the enzymes of yeast, and are, consequently, to be regarded as β-glucosides.

l-Camphorglycuronic acid in the anhydrous state has m. p. 128—129° (compare Magnus-Levy, Abstr., 1907, i, 228); it is not hydrolysed by dried yeast extract, but when acted on by emulsin yields camphorol and is therefore, undoubtedly, a β-glucoside. W. H. G.

Pinene Hydrohalides and their Transformation into Hydrocarbons of the Santene and Cyclene Types. IWAN L. KONDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 338—355).—The author discusses his own work (compare Abstr., 1908, i, 665; 1909, i, 311, 502, 942) and that of other investigators, more especially on the pinene hydrochlorides, and draws the following conclusions: The solid *d*- and *l*-pinene hydrochlorides do not possess definite optical rotations, and represent mixtures of two antipodes with preponderance of one or the other form. When hydrogen chloride is removed with avoidance of all isomerising influences, the pure *d*-hydrochloride yields almost pure bornylene, whilst the pure *l*-hydrochloride gives camphene (cyclene ?), probably formed as a result of the action of conditions of isomerisation on the cyclene or bornylene representing the first product of the reaction. It is possible that both the hydrochlorides undergo preliminary transformation into *iso*bornyl hydrochloride.

On treatment with halogen hydracids, pinene yields principally two classes of derivatives, firstly, real borneol derivatives, and secondly, real fenchyl compounds, each of these classes of compounds then giving further independent derivatives, such as bornylene, cyclene, *iso*cyclene, fenchobornylene, fenchocyclene, and fencho*iso*cyclene. A second group comprises methene-camphene and *iso*camphene, which are products of isomeric change of compounds of the first series.



When methene-camphene is oxidised, for example, by dilute permanganate solution, it seems to undergo hydration to a tertiary alcohol, which decomposes, giving cyclene, the latter then combining with water to form the annexed secondary alcohol; this, by loss of water, is converted into *iso*camphene. T. H. P.

Essential Oils. SCHIMMEL & Co. (*Bericht*, April, 1910).—The leaves of *Aegle marmalos* yielded 0·6% of a pale yellow oil, D^{25} 0·856, a_D^{26} +10·71°, boiling principally below 130°, and having saponification number 10·6.

Java citronella oil contained about 0·2% of citral. Citronella oil from German New Guinea had D^{15} 0·8964, a_D, −1°20′, and contained 78% of geraniol and citronellal.

Cypress camphor is identical with cedar camphor, and has $[a]_D$ +10°5′ in chloroform.

Dill oil from Galicia had D^{15} 0·9425, a_D +48°16′, n_D^{20} 1·50775, and was not completely soluble in 80% alcohol, and probably contained fennel oil.

Bergamot oil from Sicily had D^{15} 0·8829, a_D +15°20′, acid number 1·5, ester number 100·7, contained 5·8% of non-volatile matter, and gave a clear solution with 0·5 or more volumes of 90% alcohol. Terpinyl acetate has been found as an adulterant recently in bergamot oils, and may best be detected by quantitative fractional distillation of the oil and examination of the optical rotation and refractive index of each portion (compare Umney, *Chem. and Drugg.*, 1909, **75**, 411, 487, 522).

A résumé of the results of Chace's investigations on the occurrence

of pinene in lemon oil (*Circ.* No. 46, *Bur. Chem. U.S.A. Dept. Agric.*) is given and of the various criticisms of these results that have appeared in technical journals.

According to Swenholt, oils distilled from the leaves and twigs of the Coniferous trees named below had the following constants: *Picea Engelmanni*, D 0·8950, α_D $+1°55'38''$ (in a 5-cm. tube), saponification number 24·15, corresponding with 8·5% of bornyl acetate: this oil smells of camphor. *Pinus murrayana* had saponification number 51·87, equal to 18% of bornyl acetate. *P. flexilis* had D 0·8670, α_D $+4°28'$ (in a 5-cm. tube), saponification number 43·14, corresponding to 15% of bornyl acetate. *P. edulis* had D 0·8653, α_D $-3°36'58''$ (in a 5-cm. tube), saponification number 17·55, equivalent to 6% bornyl acetate.

Lemon-grass oils from Jalpaiguri, India, had the following constants: I. Grass cut in July, no flowers: D^{15} 0·8924 to 0·8954, α_D $-0°28'$ to $-0°49'$, aldehydes (by acid bisulphite process) 87—90%. II. Grass cut in September, no flowers: D^{15} 0·8925, α_D $-0°53'$, aldehydes 85·5%. III. Leaves of grass, in flower: D^{15} 0·8916, α_D $-1°5'$, aldehydes 86·0%. IV. Flowers only: D^{15} 0·8897, α_D $-1°15'$, aldehydes 83%. A lemon-grass oil from Eastern Bengal had D^{15} 0·9122, α_D ± 0, aldehydes 83%. A specimen from New Guinea contained 65% of aldehydes, and had D^{15} 0·8857, α_D $-0°40$; both the latter oils were of the "insoluble" type.

Mosla japonica herb furnished, according to Murayama, 2% of oil containing *p*-cymene and 50% of carvacrol.

Myrtle oil from Cyprus had D^{15} 0·9174, α_D $+8°11'$, n_D^{20} 1·46357, acid number 0·3, ester number 20·9, acetyl ester number 63·9, and was soluble in one or more volumes of 80% alcohol.

Oil from sweet orange flowers, grown in Southern France, had D^{15} 0·8686, α_D $+45°16'$, n_D^{20} 1·47352, acid number 1·8, ester number 16·7, and was soluble in 0·5 volume of 90% alcohol, becoming opalescent with 5 volumes.

A so-called "petit-grain" oil, distilled from leaves only in Dominica, had D^{15} 0·8531, α_D $+43°36'$, acid number 1·2, ester number 6·1, and was soluble in 4 to 5 volumes of 90% alcohol with slight opalescence.

Rosemary oil from Greece had D^{15} 0·9148, α_D $+1°37'$, and was soluble in one or more volumes of 80% alcohol.

Celery seed oil had D^{15} 0·8946, α_D $+67°51'$, n_D^{20} 1·48566. The terpene fraction had b. p. 175—180°, and consisted mainly of *d*-limonene. The alcohol fraction had b. p. 195—230°, and was not examined. The portion boiling from 110—130° under 9 mm. pressure consisted mainly of a sesquiterpene (compare Ciamician and Silber, Abstr., 1897, i, 291, 483), which it is proposed to call d-*selinene*. The latter could not be obtained pure by fractionation. The crude sesquiterpene was converted into the *dihydrochloride*, m. p. 72—74°, $[\alpha]_D$ $+18°$ in chloroform, and this, on treatment with sodium ethoxide, yielded a hydrocarbon, b. p. 268—272°, D^{15} 0·9232, D^{20} 0 9196, α_D $+49°30'$, n_D^{20} 1·50483, which was probably identical with the original selinene, since on treatment with hydrogen chloride it furnished the dihydrochloride melting at 72—74°. No other crystalline derivatives could be obtained. The oil also contained phenols, sedanolide, and sedanonic acid, as found by Ciamician and Silber (*loc. cit.*).

A hydrocarbon fraction of star anise oil had b. p. 63°/13·5 mm., D^{15} 0·8601, α_D −22°31′, n_D^{20} 1·47226, and was found to contain, in addition to the constituents already observed, *p*-cymene and a mixture of *l*-α- and -β-phellandrene. Cineol, safrole, and terpineol were also noted in the alcohol fraction (compare Oswald, Abstr., 1891, i, 957, and Tardy, Abstr., 1903, i, 46).

Two storax oils proved to be merely styrene perfumed with benzyl benzoate; one of them also contained pinene.

"Yellow pine oil," obtained by the steam distillation of yellow pine "stumps," had D^{15} 0·9536, α_D −3°26′, n_D^{20} 1·48537, acid number 0, ester number 14·2, acetyl ester number 161·4, and total alcohol content 58%. *l*-α-Terpineol was isolated from this oil in a pure state (compare Teeple, Abstr., 1908, i, 355). The other constituents were α- and β-pinene, camphene, *l*-limonene, dipentene, γ-terpinene, *l*-borneol, cineol, *i*-fenchyl alcohol, camphor, and methylchavicole. The last four are new constituents as regards oils derived from species of the *Abietineae*, whilst fenchyl alcohol has not been observed in any natural essential oil previously. The oil also contained a *stereoisomeride* of *i*-fenchyl alcohol: this had b. p. 202—203°, D^{15} 0·9655, α_D +1°10′, n_D^{20} 1·47465; on oxidation it yielded *i*-fenchone, and on dehydration a fenchene, having b. p. 154—156°, D^{15} 0·8669, α_D −2°38′, n_D^{20} 1·47056. The *phenylurethane* of the alcohol had m. p. 94—95°, and the *phthalic acid* ester, m. p. 142—144°.

A résumé of recent work on the detection of adulterants in turpentine oil is given (compare Marcusson, *Chem. Zeit.*, 1909, **33**, 966, 978, 985; Herzfeld, *loc. cit.*, 1081; Nicolardot and Clement, *Compt. rend.*, 1909, **49**, 572; Mansier, this vol., ii, 1056; Darmois, Abstr., 1908, ii, 747). *Pinus ponderosa* turpentine, from the Philippines, gave, according to Richmond, 23·4% of turpentine oil, which had D_{30}^{30} 0·8593, α_D^{30} +26·5°, n_D^{30} 1·4656, and boiled mostly from 154° to 165·5°.

Ylang-ylang oil, distilled in Réunion, had D^{15} 0·939, α_D −64°, n_D^{20} 1·510, saponification number 97, and contained benzoic acid 9%, acetic acid 4·0%, alcohols (linalool and geraniol) 25·5%, and cadinene, 31%.

Cinnamomum tamala leaf oil had D^{15} 1·0257, α_D +16°37′, n_D^{20} 1·52596, eugenol 78%, and was soluble in 1·2 or more volumes of 70% alcohol. The oil, after removal of eugenol, had α_D +66°40′, and contained *d*-α-phellandrene.

Guava-leaf oil from Cuba had D^{15} 0·9157, α_D −10°5′, n_D^{20} 1·49638, acid number 2·0, ester number 6·4, and was soluble in 10 volumes of 90% alcohol.

Mentha sylvestris oil, from Cyprus, had D^{15} 0·9701, α_D +31°30′, n_D^{20} 1·49544, acid number 2·4, ester number 20·9, acetyl ester number 171·4, and was soluble in 3 volumes of 70% alcohol. It contained pulegone, menthol, and probably carvacrol. T. A. H.

[**Carrot Oil, the Ethereal Oil from Daucus Carota.**] ERWIN RICHTER (*Ber.*, 1910, **43**, 958).—The author will reply to Deussen's criticisms (*ibid.*, 523) of his work (Abstr., 1909, i, 943) when the promised fuller details are published. C. S.

Theory of the Cold Vulcanisation of Rubber. F. Willy Henrichsen and Erich Kindscher (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 202—209. Compare this vol., ii, 62).—Experiments have been made to determine the nature of the process of the vulcanisation of rubber with sulphur chloride. Weighed amounts of purified para-rubber were subjected to the action of varying quantities of a dry benzene solution of sulphur chloride in stoppered flasks for a period of three to four weeks, at the end of which time the amount of unchanged sulphur chloride in the clear solution was determined. The observed changes in the concentration of the sulphur chloride indicate that a definite compound is formed of the composition

$$(C_{10}H_{16})_2,S_2Cl_2.$$

Direct analysis of the substance which separates out from the benzene solution gave quantities of sulphur largely in excess of that required by the formula, but this is probably due to decomposition of the sulphur chloride in the processes of separation and purification.

When treated for several days with an alcoholic solution of sodium hydroxide, the above compound loses two molecules of hydrogen chloride, and a dark brown, hard substance of the composition

$$C_{20}H_{30}S_2$$

is obtained. In consequence of the separation of free sulphur, the analytical data for the amount of sulphur present are from 1 to 2% higher than that required by the formula.

The authors consider that ordinary vulcanised rubber consists of a solid or semi-solid solution of para-rubber and the sulphur chloride additive compound, in which variable amounts of adsorbed sulphur are contained. H. M. D.

Phylloporphyrin. Léon Marchlewski (*Annalen*, 1910, **372**, 252—253).—Polemical. A reply to Willstätter and Fritsche (this vol., i, 126). W. H. G.

Phylloporphyrin. Richard Willstätter (*Annalen*, 1910, **372**, 253).—Polemical. A reply to Marchlewski (compare preceding abstract). W. H. G.

Colouring Matter of Tomatoes. Richard Willstätter and Heinrich H. Escher (*Zeitsch. physiol. Chem.*, 1910, **64**, 47—61. Compare Schunck, *Proc. Roy. Soc.*, 1903, **72**, 165; Montanari, Abstr., 1905, i, 293.)—Lycopene, the colouring matter of tomatoes, and carrotene (Abstr., 1907, i, 865) have the same molecular formula, $C_{40}H_{56}$, but are not identical. Lycopene is most readily obtained from preserved tomatoes, together with a small amount of carrotene. It crystallises from light petroleum or a mixture of alcohol and carbon disulphide in pale or dark carmine-red, felted prisms. Its solutions in carbon disulphide have a bluish-red colour, whereas carrotene yields reddish-yellow solutions. It has m. p. 168—169° (corr.) [Montanari (*loc. cit.*) gives 170° (uncorr.)], and is less soluble than carrotene in ether, alcohol, carbon disulphide, or light petroleum. A dilute alcoholic solution has two absorption bands: $\lambda = 510$—499 and $\lambda = 480$—468. Carbon disulphide solutions have two absorption bands,

in the green and one in the blue. Lycopene absorbs oxygen much more readily than does carrotene, and to the extent of 32·5%. Its di-iodide, $C_{40}H_{56}I_2$, forms a dark green, gelatinous precipitate. A carbon disulphide solution of lycopene reacts with bromine, yielding the *compound*, $C_{40}H_{44}Br_{26}$, which sinters at 148° and decomposes at 174°.

When carrotene is exposed to oxygen, an odour of violet roots is noticed. In addition to the di-iodide described by Willstätter and Mieg, carrotene yields the *compound*, $C_{40}H_{56}I_3$, which crystallises in dark violet plates with a metallic lustre, m. p. 136—137°. Carrotene and bromine yield the compound $C_{40}H_{36}Br_{22}$, which decomposes at 171—174°. Xanthophyll yields a similar bromide, $C_{40}H_{40}Br_{22}$.

J. J. S.

The Action of Zinc Oxide on Tannin. LEO F. ILJIN (*J. pr. Chem.*, 1910, [ii], **81**, 327—328. Compare Abstr., 1909, i, 821).—If 100 grams of tannin are dissolved in a litre of water, boiled for four hours with 100 grams of zinc oxide, and filtered, the filtrate is slightly coloured and does not react with ferric chloride. The residue, after decomposition with sulphuric acid, yields 35 grams of gallic acid, and 32 grams of the same compound as was obtained by the action of zinc dust on tannin.

C. H. D.

Basic Properties of Oxygen. Compounds of Dimethylpyrone and the Halogen Hydrides. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1910, **32**, 542—547).—In an earlier paper (Abstr., 1908, i, 596) it has been shown that certain substances regarded by Baeyer and Villiger (Abstr., 1901, i, 658; 1902, i, 112, 355) as quadrivalent oxygen compounds are either solid solutions or molecular compounds containing alcohol of crystallisation. Since it is possible that the salts of dimethylpyrone might be considered as compounds containing "acid of crystallisation," some of these have now been examined over a wide range of temperature.

Conductivity measurements of dimethylpyrone in liquid hydrogen bromide at $-78°$ and in liquid hydrogen chloride at $-100°$ have been made, and the results are tabulated and plotted as curves. It is shown that the molecular conductivity increases with the concentration, and the conclusion is therefore drawn that complex ions are formed.

In addition to the salts described by Collie and Tickle (Trans., 1899, **75**, 710), the following have now been obtained: $C_7H_8O_2,3HCl$, m. p. $-25°$; $C_7H_8O_2,4HBr$, m. p. $-59°$; $C_7H_8O_2,2HBr$, m. p. $-2°$; $C_7H_8O_2,4HI$, m. p. $-42°$; $C_7H_8O_2,2HI$, m. p. 7°. Weinland and Reischle (Abstr., 1908, i, 974) have described two dimethylpyrone hydrofluorides, but experiments which are now described indicate that, if such compounds are formed, they are very unstable.

Suggestions are made with reference to the constitution of the compounds of dimethylpyrone with the halogen hydrides.

E. G.

o-ψ-Bromides from o-Hydroxystyrene, their Transformation Products, and Conversion into Coumaran Derivatives. KARL FRIES and PAUL MOSKOPP (*Annalen*, 1910, **372**, 187—204).—An

investigation on the ψ-bromides of *o*-ethylphenol which result from the action of bromine on *o*-hydroxystyrene.

3 : 5-*Dibromo-2-hydroxystyrene bromide*, $OH\cdot C_6H_2Br_2\cdot CHBr\cdot CH_2Br$, is formed by the action of bromine on a solution of *o*-hydroxystyrene in glacial acetic acid; it crystallises in aggregates of plates, m. p. 108°, and is converted (1) by acetic anhydride and concentrated sulphuric acid into the *acetate*, $C_{10}H_8O_2Br_4$, white needles, m. p. 74°; (2) by boiling acetic anhydride and anhydrous sodium acetate into β : 3 : 5-*tribromo-a* : 2-*diacetoxyethylbenzene*,

$$OAc\cdot C_6H_2Br_2\cdot CH(OAc)\cdot CH_2Br,$$

colourless plates, m. p. 90°; (3) by methyl alcohol, under pressure at 100°, into β : 3 : 5-*tribromo-2-hydroxy-a-methoxyethylbenzene*,

$$OH\cdot C_6H_2Br_2\cdot CH(OMe)\cdot CH_2Br,$$

large, white, rhombic crystals, m. p. 58°, which, when boiled with glacial acetic acid, acetic anhydride, and sodium acetate, yield 4 : 6-*dibromo-2-methoxycoumaran*, $C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{CH(OMe)}{O}}{>}CH_2$, white, spear-shaped needles, m. p. 95°; (4) by zinc and hydrochloric acid into 3 : 5-*dibromo-2-hydroxystyrene*, $C_8H_6OBr_2$, slender needles, m. p. 58°, the *acetate* of which, $C_{10}H_8O_2Br_2$, crystallises in needles, m. p. 51°; and (5) by hot glacial acetic acid and anhydrous sodium acetate into 4 : 6-*dibromo-2-acetoxycoumaran*, $C_{10}H_8O_3Br_2$, rhombic plates, m. p. 98—99°, which when treated with an aqueous-alcoholic solution of sodium hydroxide yields 4 : 6-*dibromo-2-hydroxycoumaran*, $C_8H_6O_2Br_2$, slender needles, m. p. 120°; the latter substance, dissolved in light petroleum, is converted by phosphoric oxide into 4 : 6-dibromo-coumarone (compare Simonis and Wenzel, Abstr., 1900, i, 231).

4 : 6-*Dibromo-2-coumaranone*, $C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{CO}{O}}{>}CH_2$, is formed by the action of chromic acid on 4 : 6-dibromo-2-hydroxycoumaran; it crystallises in pale yellow needles, m. p. 145°, and (1) condenses with isatin in glacial acetic acid containing concentrated sulphuric acid, yielding 1-(4 : 6)-*dibromocoumaranonyl-3-indole*,

$$C_6H_2Br_2{<}{\genfrac{}{}{0pt}{}{CO}{O}}{>}C{:}C{<}{\genfrac{}{}{0pt}{}{C_6H_4}{CO}}{>}NH,$$

brownish-red needles, m. p. above 280°; (2) is converted by glacial acetic acid and sodium nitrite into 4 : 6-*dibromo-1-oximinocoumaranone*, $C_8H_3O_3NBr_2$, compact, glistening, yellow prisms, m. p. 186° (decomp.), which when boiled with acetic acid and hydrochloric acid yields 3 : 5-*dibromo-2-hydroxyphenylglyoxylic acid*,

$$OH\cdot C_6H_2Br_2\cdot CO\cdot CO_2H,$$

compact, yellow needles, m. p. 142° (decomp.); the latter compound condenses with *o*-phenylenediamine, yielding the corresponding *quinoxaline* derivative, which crystallises in needles, m. p. above 280°.

a : β : β : 3 : 5-*Pentabromo-2-hydroxyethylbenzene*,

$$OH\cdot C_6H_2Br_2\cdot CHBr\cdot CHBr_2,$$

is formed by heating 3 : 5-dibromo-2-hydroxystyrene bromide with bromine under pressure at 100°; it crystallises in white nodules, m. p. 141°; the *acetyl* derivative, $C_{10}H_7O_2Br_5$, forms crystalline nodules, m. p. 128°. The pentabromo-compound is converted (1) by hot glacial acetic acid and anhydrous sodium acetate into β : β : 3 : 5-*tetrabromo-*

2-hydroxy-α-acetoxyethylbenzene, $C_{10}H_8O_3Br_4$, plates, m. p. 126°; (2) by hot acetic anhydride and anhydrous sodium acetate into β : β : 3 : 5-*tetrabromo-α* : *2-diacetoxyethylbenzene*, $C_{12}H_{10}O_4Br_4$, small, glistening, white plates, m. p. 115°; (3) by methyl alcohol at 100° into β : β : 3 : 5-*tetrabromo-2-hydroxy α-methoxyethylbenzene*, $C_9H_8O_2Br_4$, large, white plates, m. p. 110°; and (4) by zinc and hydrochloric acid into ω : 3 : 5-*tribromo-2-hydroxystyrene*, $C_8H_5OBr_3$, crystalline nodules, m. p. 95°, the *acetate* of which, $C_{10}H_7OBr_3$, crystallises in small prisms, m. p. 132°; the *methyl ether* crystallises in leaflets, m. p. 64°, and when oxidised yields 3 : 5-dibromo-2-methoxybenzoic acid. W. H. G.

o-ψ-Bromides of Thymol and 4-Hydroxy-1-methyl-3-*iso*propylbenzene (4-Hydroxy-*m*-cymene), their Transformation Products, and Conversion into Coumaran and Coumaranone Derivatives. Karl Fries (*Annalen*, 1910, **372**, 205—236).—The bromination of 2-hydroxy-α : 4-dimethylstyrene leads to the formation of a hexabromo-ψ-bromide of thymol, identical with the hexabromothymol obtained by von Baeyer and Seuffert (Abstr., 1901, i, 216) from menthone (compare Fries and Fickewirth, Abstr., 1908, i, 160). The formulæ assigned by the first-named investigators to this compound and its derivatives are incorrect; it is shown that the hexabromo-compound has the constitution:

$$\begin{array}{l} \text{CBr:CH—C}\cdot\text{CBr(CH}_2\text{Br)}\cdot\text{CHBr}_2. \\ \text{CMe:CBr}\cdot\text{C}\cdot\text{OH} \end{array}$$

[With W. Volk.]—α : β : β : 2 : 6-*Pentabromo-3-hydroxy-1-methyl-α-bromomethyl-4-ethylbenzene* is most readily prepared by the action of bromine on a solution of thymol in chloroform; it is converted by sodium hydrogen carbonate into β : β : 3 : 5-*tetrabromo-2-hydroxy-4-methyl-α-bromomethylstyrene*, m. p. 106° (102°: von Baeyer and Seuffert, *loc. cit.*), and by an aqueous-alcoholic solution of sodium hydroxide into 1 : 4 : 6-*tribromo-5-methyl-2-bromomethylcoumarone*, m. p. 179°. The latter substance is converted by a solution of hydrogen bromide in glacial acetic acid into 1 : 1 : 4 : 6-*tetrabromo-5-methyl-2-methylene-coumaran*, $C_6HMeBr_2{<}{\genfrac{}{}{0pt}{}{C(:CH_2)}{O}}{>}CBr_2$, which crystallises in prisms, m. p. 140°, and is converted (1) by silver acetate in hot glacial acetic acid into 1 : 4 : 6-*tribromo-1-acetoxy-5-methyl-2-methylenecoumaran*,

$C_{12}H_9O_3Br_3$,

small needles, m. p. 138°; (2) by methyl alcohol under pressure at 100° into 1 : 4 : 6-*tribromo-1-methoxy-5-methyl-2-methylenecoumaran*,

$C_{11}H_9O_2Br_3$,

which forms slender needles, m. p. 148°, and, when treated with cold concentrated sulphuric acid, yields 4 : 6-*dibromo-5-methyl-2-methylene-coumaran-1-one*, $C_6HMeBr_2{<}{\genfrac{}{}{0pt}{}{C(:CH_2)}{O}}{>}CO$, slender, white needles, m. p. 145°; the acid, of which the latter compound is the lactone, could not be isolated, but the *methyl* ester was prepared; it forms small needles, m. p. 119°.

β : β : 3 : 5-Tetrabromo-2-hydroxy-4-methyl-α-bromomethylstyrene is converted by methyl alcohol at 100° into β : 3 : 5-*tribromo-2-hydroxy-β-methoxy-4-methyl-α-bromomethylstyrene*,

$$OH\cdot C_6HMeBr_2\cdot C(CH_2Br):CBr\cdot OMe,$$

which crystallises in long prisms, m. p. 85°, and, when treated with hydrogen iodide in glacial acetic acid, yields *β : 3 : 5-tribromo-β-iodo-2-hydroxy-4-methyl-α-bromomethylstyrene*, $C_{10}H_7OBr_4I$, long, glistening prisms, m. p. 119°; the *methyl ether* of the former compound,

$$C_{12}H_{12}O_2Br_4,$$

crystallises in plates, m. p. 89°, and is converted (1) by cold concentrated sulphuric acid into 4 : 6-dibromo-5-methyl-2-methylenecoumaranone, *αβ-3 : 5-tetrabromo-2-methoxy-α-p-tolylpropionic acid*, $OMe\cdot C_6HMeBr_2\cdot CBr(CH_2Br)\cdot CO_2H$, small, slender, white needles, m. p. 235°, and *β : β : 3 : 5-tetrabromo-2-methoxy-4-methyl-α-bromomethylstyrene*, $OMe\cdot C_6HMeBr_2\cdot C(CH_2Br):CBr_2$, small, colourless plates, m. p. 123°; (2) by dilute nitric acid into *3 : 5-dibromo-2-methoxy-4-toluic acid*, $C_9H_8O_3Br_2$, needles, m. p. 196°, the *methyl* ester of which, $C_{10}H_{10}O_3Br_2$, forms prisms, m. p. 55°.

[With P. Moskopp.]—*4-Hydroxy-m-cymene*, $C_{10}H_{14}O$, is prepared by reducing 2-hydroxy-α : 5-dimethylstyrene with sodium and alcohol; it crystallises in slender needles, m. p. 35°, b. p. 227°/750 mm.; the *benzoate*, $C_{17}H_{18}O_2$, forms large prisms, m. p. 60°.

α : β : β : 5-Tetrabromo-4-hydroxy-1-methyl-α-bromomethyl-3-ethylbenzene, $OH\cdot C_6H_2MeBr\cdot CBr(CH_2Br)\cdot CHBr_2$, prepared by acting on 2-hydroxy-α : 5-dimethylstyrene or the hydroxy-*m*-cymene just described with bromine in chloroform, forms stellate aggregates of compact, glistening needles, m. p. 131°; the *acetate*, $C_{12}H_{11}O_2Br_5$, forms white, glistening crystals, m. p. 136°. The former compound is converted (1) by zinc and hydrochloric acid into *5-bromo-6-hydroxy-α : 3-dimethylstyrene*, $C_{10}H_{11}OBr$, an oil, b. p. 129—134°/15 mm.; (2) by aqueous acetone into *β : β : 5-tribromo-6-hydroxy-3-methyl-α-bromomethylstyrene*, $C_{10}H_8OBr_4$, which crystallises in glistening, white plates, m. p. 101°, yields an *acetate*, $C_{12}H_{10}O_2Br_4$, plates, m. p. 95°, and is converted by alkali into *1 : 6-dibromo-4-methyl-2-bromomethylcoumarone*,

$$C_6H_2MeBr\genfrac{<}{>}{0pt}{}{C(CH_2Br)}{O}CBr,$$

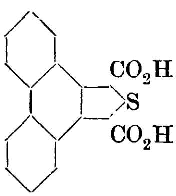
white needles, m. p. 128°; (3) by methyl alcohol at 100° into *β : 5-dibromo-6-hydroxy-β-methoxy-3-methyl-α-bromomethylstyrene*,

$$C_{11}H_{11}O_2Br_3,$$

which crystallises in slender, white needles, m. p. 135°, forms an *acetate*, white cubes, m. p. 66°, and, when acted on by hydrogen iodide in glacial acetic acid, yields *β : 5-dibromo-β-iodo-6-hydroxy-3-methyl-α-bromomethylstyrene*, $OH\cdot C_6H_2MeBr\cdot C(CH_2Br):CBrI$, glistening prisms, m. p. 115°; and (4) by ethyl alcohol into the corresponding *ethoxy*-compound, $C_{12}H_{13}O_2Br_3$, small plates, m. p. 68°. W. H. G.

Synthetical Experiments with Esters of Thiodiglycollic Acid. Oscar Hinsberg (*Ber.*, 1910, **43**, 901—906).—In ethyl thiodiglycollate, $S\cdot(CH_2\cdot CO_2Et)_2$, both methylene groups are placed between two negative groups. They are found to be strongly negative, and very readily react with α-dicarbonyl compounds: for example, *o*-diketones, *o*-quinones, *o*-keto-esters, and oxalic acid esters. As the α-carbethoxy-group has only a relatively faint activating influence, the α-sulphur atom is proved to belong also to the activating atomic groups.

Ethyl thiodiglycollate reacts with benzil in presence of sodium, forming a product which, after hydrolysis of the ester, crystallises in colourless, glistening needles. The 3:4-*diphenylthiophen*-2:5-*dicarboxylic acid* formed decomposes at 300° when heated, forming 3:4-diphenylthiophen.



Phenanthraisothiophendicarboxylic acid (annexed constitution), prepared in a similar manner from phenanthraquinone, crystallises in minute, yellow needles, decomp. 270°, whereby *phenanthraisothiophen* is formed; this separates from alcohol or chloroform in light yellow plates, m. p. 163°.

Methyl 3 : 4-*dihydroxythiophen*-2 : 5-*dicarboxylate*,

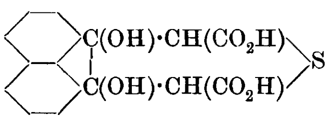
$$S<\begin{matrix}C(CO_2Me)\colon C\cdot OH \\ C(CO_2Me)\colon C\cdot OH\end{matrix}$$

prepared by the interaction of methyl thiodiglycollate and ethyl oxalate in presence of sodium methoxide, crystallises in colourless needles, m. p. 178°. The alkali salts are bright yellow. In alcoholic solution the ester gives a blue coloration with ferric chloride, changing to red on the addition of sodium carbonate. The ester is hydrolysed with difficulty. The corresponding *ethyl* ester forms colourless needles, m. p. 134°.

Ethyl hydrogen 3-*hydroxy*-4-*methylthiophen*-2 : 5-*dicarboxylate*,

$$S<\begin{matrix}C(CO_2Et)\colon C\cdot OH \\ C(CO_2H)\colon CMe\end{matrix},$$

prepared by the interaction of ethyl thiodiglycollate, ethyl pyruvate, and sodium methoxide, crystallises from dilute alcohol in colourless needles, m. p. 233°. When boiled with dilute sodium hydroxide, 3-*hydroxy*-4-*methylthiophen*-5-*carboxylic acid* is obtained in very slender, long needles, m. p. 184°.



Dihydroxytetrahydroacenaphthaisothiophendicarboxylic acid (annexed constitution), obtained by the interaction of ethyl thiodiglycollate and acenaphthenequinone, forms small, colourless needles, decomp. 250°.

E. F. A.

Gnoscopine (*r*-Narcotine). PAUL RABE and ANDREW MCMILLAN (*Ber.*, 1910, **43**, 800—804. Compare Abstr., 1907, i, 790; W. H. Perkin and Robinson, Proc., 1910, **26**, 46).—The properties and reactions of gnoscopine all point to the conclusion that it is *r*-narcotine. It is obtained by heating narcotine with absolute alcohol at 175° for six hours, or with dilute alcohol in a reflux apparatus during eight days. The *hydrochloride*, $C_{22}H_{23}O_7N,HCl$, crystallises in colourless needles, has m. p. 238° (decomp.), and is hydrolysed by water. The *picrate* has m. p. 185°, and the *picrolonate*, 232° (decomp.). When oxidised with nitric acid, both narcotine and gnoscopine yield cotarnine, and when heated with water at 140°, both alkaloids yield hydrocotarnine.

It has been found possible to resolve gnoscopine methiodide by means of silver bromocamphorsulphonate.

Narcotine methyl bromocamphorsulphonate, $C_{33}H_{40}O_{11}NBrS$, crystallises in colourless needles, has m. p. 231° (decomp.), and $[\alpha]_D^{23}$ +101°.

J. J. S.

Conversion of Guanine into Xanthine by means of Hydrochloric Acid. EMIL FISCHER (*Ber.*, 1910, **43**, 805—806).—Guanine (1 gram) gives a 60—70% yield of xanthine when heated with 100 c.c. of 25% hydrochloric acid for thirty-two hours in a reflux apparatus.

The decomposition is analogous to the formation of dialkylmalonylcarbamides and ammonia from dialkylmalonylguanidines. J. J. S.

Behaviour of Histidine towards Picrolonic Acid. P. BRIGL (*Zeitsch. physiol. Chem.*, 1910, **64**, 337—340).—Histidine and picrolonic acid yield the yellow monopicrolonate, $C_6H_9O_2N_3,C_{10}H_8O_5N_4$, whereas the mono- and di-hydrochloride of the base yield the orange dipicrolonate, $C_6H_9O_2N_3,2C_{10}H_8O_5N_4$, even when only one gram-molecule of picrolonic acid is used. The yields when the hydrochlorides are made use of are poor, and the method cannot be employed for estimating histidine. The dipicrolonate can also be prepared from the free base if an excess of picrolonic acid is used. J. J. S.

Derivatives of Histidine. HERMANN PAULY (*Zeitsch. physiol. Chem.*, 1910, **64**, 75—81).—p-*Nitrobenzoylhistidine*,

$$C_6H_8N_3O_2\cdot CO\cdot C_6H_4\cdot NO_2,$$

prepared by adding a benzene solution of *p*-nitrobenzoyl chloride and an aqueous solution of sodium hydroxide to a well-stirred ice-cold aqueous solution of histidine hydrochloride, crystallises in slender needles, m. p. 251—252°. In the preparation of histidine anhydride from histidine methyl ester (Fischer and Suzuki, Abstr., 1905, i, 121; 1906, i, 73), in addition to the *l*-anhydride a certain amount of the less soluble *d*-*l*-anhydride is formed. The *l*-anhydride has m. p. 328° in a closed evacuated tube; it crystallises with $2\frac{1}{2}H_2O$, which it loses at 140°. Its solution in *N*-hydrochloric acid has $[\alpha]_D^{20}$ −66·24°. The anhydride yields insoluble *silver*, $C_{12}H_{12}O_2N_6Ag_2$, and *mercuric* salts.

d-l-*Histidine anhydride* has also m. p. 328°. A better yield of the racemic anhydride is obtained when histidine ethyl ester is heated to 160° for several hours. J. J. S.

Synthesis of Hordenine. EUGÈNE LÉGER (*Bull. Soc. chim.*, 1910, [iv], **7**, 172—173. Compare Abstr., 1906, i, 204, 761).—A claim for priority over Barger (Trans., 1909, **95**, 2193).

W. O. W.

Constants of the First and Second Dissociations of Quinine. J. O. WAKELIN BARRATT (*Zeitsch. Elektrochem.*, 1910, **16**, 130—132).—The concentration of the hydroxyl ions in a solution of quinine was measured by adding phenolphthalein to it, and then mixing solutions of disodium hydrogen phosphate and trisodium phosphate with phenolphthalein until the same colour was obtained. Salm's determinations of the acidity of these solutions were used

(Abstr., 1904, ii, 536, and *Zeitsch. physikal Chem.*, 1906, **57**, 471). From these data the first dissociation constant is found to be $2{\cdot}6 \times 10^{-6}$ at 16—18°.

The second constant is obtained by measuring the hydrolysis of quinine dihydrochloride (also by Salm's method, using methyl-orange and hydrochloric acid for comparison). It is $1{\cdot}3 \times 10^{-10}$ at 16—18°.

T. E.

[Preparation of Dioxindols.] KALLE & Co. (D.R.-P. 217556. Compare this vol., i, 278).—Condensation products from dioxindole and 3-oxy-(1)-thionaphthen have previously been described; it is now found that the alkyloxy-dioxindoles of the general formula

$$OR{\cdot}C_6H_3\genfrac{<}{>}{0pt}{}{CH(OH)}{NH}CO, \quad R = \text{alkyl},$$

also react in this condensation, yielding brown to yellow dyes.

7-Methoxyisatin is reduced to the corresponding 4-methoxydioxindole, and this on condensation with 3-oxy-(1)-thionaphthen yields a brown powder, whilst with 6-ethoxy-3-oxy-(1)-thionaphthen-2-carboxylic acid a yellow dye is formed.

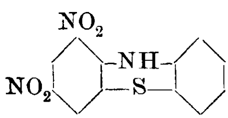
F. M. G. M.

Preparation of β-Naphthindoxyl. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216639).—When compounds of the type $\beta\text{-}C_{10}H_7{\cdot}NH{\cdot}CH_2{\cdot}CO_2R$, where R is hydrogen, alkyl or aryl groups, are heated at 100—110° with acid condensation agents, such as aluminium chloride or phosphoric oxide, β-naphthindoxyls are produced, which, on atmospheric oxidation in alkaline solution, are converted into β-naphthylindigotin.

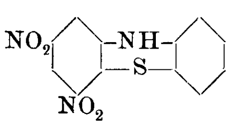
β-Naphthindoxyl, an olive-green powder when freshly-prepared, is readily soluble in organic solvents, from which it separates in greenish-yellow needles, m. p. 80—85°.

F. M. G. M.

Thiazines. R. MITSUGI, HEINRICH BEYSCHLAG, and RICHARD MÖHLAU (*Ber.*, 1910, **43**, 927—934).—Kehrmann (Abstr., 1900, i, 61) has ascribed the formula (I) to the dinitrophenthiazine obtained from *o*-aminothiophenol hydrochloride by the action of picryl chloride in presence of sodium acetate. The authors now assign the formula (II) to this compound. It is considered that the chlorine atom of picryl chloride attacks, not the amino-group, but the sulphydryl group of *o*-aminothiophenol.



(I.)



(II.)

When molecular proportions of dibenzoyl-*m*-diamino-*m*-thiocresol and picryl chloride interact, *trinitrophenyl dibenzoyldiaminotolyl sulphide*, $C_6H_2Me(NHBz)_2{\cdot}S{\cdot}C_6H_2(NO_2)_3$, is formed. This separates in orange-yellow crystals, m. p. 234° (decomp.). It dissolves in alcoholic sodium hydroxide in the cold with a blood-red coloration, forming *dinitrodibenzoylaminophenotoluthiazine*,

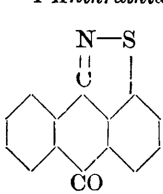
$$C_6H_2Me(NHBz)\genfrac{<}{>}{0pt}{}{NBz}{S}C_6H_2(NO_2)_2,$$

which separates from acetic acid in brownish-yellow, glistening plates. On boiling with alcoholic sodium hydroxide, the benzoyl group attached to the nitrogen atom of the thiazine ring is eliminated, and *dinitrobenzoylaminophenotoluthiazine* is formed, crystallising in deep blackish-violet, glistening prisms.

On reduction with stannous chloride, *diaminobenzoylaminophenotoluthiazine*, $C_6H_2Me(NHBz){<}{}^{NH}_{-S-}{>}C_6H_2(NH_2)_2$, is formed. The *stannichloride* forms concentrically-grouped, long needles. On oxidation, it is converted into *diaminobenzoylaminophenotoluazothionium chloride*. The *ferrichloride*, $C_{20}H_{17}ON_4SCl,FeCl_3+H_2O$, separates in lustrous, deep blackish-violet prisms. It dissolves in alcohol with an olive-yellow coloration, and forms an almost insoluble *platinichloride* and *dichromate*. The *diacetate* forms faintly yellow-coloured, long needles, and in presence of aniline it is converted by ferric chloride into 7-*benzoylamino*-2 : 4-*diacetyldiamino*-3-*anilinophentoluazothionium* 6-*chloride*, $C_6H_2Me(NHBz){<}{}^{N-}_{SCl}{>}C_6H(NHAc)_2{\cdot}NHPh$, which is a black, crystalline powder. When boiled with hydrochloric acid, 2 : 4-*diamino*-7-*benzoylamino*-3-*anilinophenotoluazothionium* 6-*chloride*, a bluish-black, crystalline powder, is obtained. E. F. A.

Preparation of Sulphur and Nitrogen Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 216306; 217688).—When anthraquinone-α-mercaptans are heated with aqueous ammonium hydroxide in the presence of sulphur at 100°, anthrathiazoles are obtained.

1-*Anthrathiazole* (annexed formula) crystallises from pyridine in prisms. 4-*Amino*-1-*anthrathiazole*, prepared from 4-amino-1-anthraquinone mercaptan, separates from the same solvent in yellow leaflets; it can also be obtained from 4 *amino*-1 *thiocyanoanthraquinone*, a brownish-red powder.



1-*Thiocyano*-2-*methylanthraquinone*, a yellowish-brown powder, yields 2-*methyl*-1-*anthrathiazole*, golden-yellow needles sparingly soluble in alcohol.

1 : 4-*Dithiocyanoanthraquinone*, yellowish-brown crystals (obtained from 4-chloro- or 4-nitro-1-diazoanthraquinone), yields 1-*anthrathiazole* 4-*mercaptan*, yellow needles soluble in alcohol.

1 : 5-Anthradithiazole, yellow needles, is prepared from potassium anthraquinone-1 : 5-disulphonate.

5-*Amino*-1-*anthrathiazole*, reddish-brown prisms, is obtained from sodium 5-aminoanthraquinone-1-sulphonate.

The condensation and reduction of sodium 1-chloro-4-nitroanthraquinone-8-sulphonate yields 4-*amino*-1-*anthrathiazole*-8-*sulphonic acid*.

These substances all give characteristic colour reactions with concentrated sulphuric acid, sodium hydroxide, and formaldehyde, which are tabulated in the patent.

In the second patent (217688) it is stated that the presence of free sulphur is not necessary for the preparation of anthrathiazoles.

1-Anthrathiazole can be prepared by heating α-thiocyanoanthraquinone with ammonia at 140° under pressure:

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot SCN + NH_3 = \begin{matrix}C_6H_4\cdot C\!\!=\!\!=\!\!=\!\!N\\ | \qquad\quad | \\ CO\!-\!\!-C_6H_3\cdot S\end{matrix} + HCN + H_2O.$$

F. M. G. M.

Displaceability of the Nitro-group. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1910, **45**, 191—196).—The ease with which a nitro-group occurring in an aromatic compound in the ortho-position to another negative group can be displaced by an amino- or anilino-group finds an analogy in the readiness with which an amino- or anilino-group can be substituted for the ω-nitro-group of the ω-nitrobenzaldehydenitrophenylhydrazones (compare this vol., i, 192). Thus, with ammonia, the compound $NO_2\cdot CR{:}N_2H\cdot Ar\cdot NO_2$ gives

$$NH_2\cdot CR{:}N_2H\cdot Ar\cdot NO_2,$$

and with aniline, $NHPh\cdot CR{:}N_2H\cdot Ar\cdot NO_2$. The position of the nitro-group in the benzene nucleus of the phenylhydrazine residue has very little influence on these reactions, *o*-nitrophenylhydrazones reacting only slightly more slowly than the corresponding para-derivatives. The presence of a nitro-group in the phenylhydrazine residue is, however, a necessary condition for the above substitution of the ω-nitro-group, neither ω-nitrobenzaldehydephenylhydrazone nor ω : *m*-dinitrobenzaldehydephenylhydrazone being capable of reacting with alcoholic ammonia.

The analogy breaks down when the behaviour of these two classes of nitro-compounds towards sodium hydroxide or alkyloxide is considered. Thus, 1 : 2-dinitrobenzene with sodium hydroxide or methoxide gives *o*-nitrophenol or *o*-nitroanisole, whilst, under the same conditions, ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone gives always α-dinitrotetraphenyltetrazoline (*loc. cit.*).

*ω-Anilinobenzaldehyde-*p*-nitrophenylhydrazone,*

$$NHPh\cdot CPh{:}N_2H\cdot C_6H_4\cdot NO_2,$$

forms brown needles with a green reflex, m. p. 180—181°.

*ω-Anilinobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazone,*

$$NHPh\cdot CPh{:}N_2H\cdot C_6H_3Cl\cdot NO_2,$$

forms red needles, m. p. 162°. T. H. P.

Indigotin. IV. Brominated Indigotins. EUGÈNE GRANDMOUGIN (*Ber.*, 1910, **43**, 937—941. Compare this vol., i, 73, 74).—When indigotin is brominated, the halogen enters first positions 5 and 5′, then 7 and 7′, and finally 4 and 4′. 4 : 5 : 7 : 5′ : 7′-*Pentabromoindigotin,* obtained by treating indigotin with an excess of bromine in the presence of concentrated sulphuric acid, separates from boiling xylene, pyridine, or nitrobenzene in microscopic needles. By oxidation by chromic and acetic acids, it yields a mixture of di- and tri-bromoisatin, from which, after distillation with potassium hydroxide and acetylation of the resulting bromoanilines, 2 : 4 : 5-tribromoacetanilide and 2 : 4-dibromoacetanilide are derived. 4 : 5 : 7 : 4′ : 5′ : 7′-*Hexabromoindigotin,* obtained by bromination in chlorosulphonic acid, separates from boiling nitrobenzene in dark blue needles, and forms a green

solution in concentrated sulphuric acid. 4 : 5 : 7-*Tribromoisatin*, m. p. 257—258°, obtained from it by oxidation with fuming nitric and acetic acids, forms orange crystals, develops an intense violet coloration with alkali hydroxides, and yields 2 : 4 : 5-tribromoaniline by distillation with potassium hydroxide. C. S.

Preparation of Dehydroindigotin, its Homologues, and Substitution Products. LUDWIG KALB (D.R.-P. 216889).—The preparation of dehydroindigotin and its dibromo-derivative has been previously described (Abstr., 1909, i, 966). The author has now prepared *dimethyldehydroindigotin* in a similar manner from dimethylindigotin; it forms yellowish-brown tablets, m. p. 155—160° (decomp.). F. M. G. M.

Preparation of 1-*p*-Dialkylaminophenyl-2-alkyl-3-hydroxymethyl-5-pyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 217557 and 217558. Compare this vol., i, 78).—When 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone is treated in aqueous solution with chloroacetic acid and the mixture acidified, 1-p-*aminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethylpyrazolonedi*-ω-*acetic acid* is precipitated as a crystalline powder, which when heated at 235° evolves carbon dioxide, or with dilute hydrochloric acid at 140—150° during ten to twelve hours yields 1-*p*-dimethylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone.

1-p-*Cyanomethylaminophenyl*-2:4-*dimethyl*-3-*hydroxymethylpyrazolone*, an oil, is prepared by treating 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone with aqueous formaldehyde, sodium hydrogen sulphite, and subsequently warming with potassium cyanide; on methylation it yields 1-p-*methyl*-ω-*cyanomethylaminophenyl*-2 : 4-*dimethyl*-3-*hydroxymethyl*-5-*pyrazolone*, which undergoes hydrolysis with dilute sulphuric acid.

1-p-*Dimethylaminophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, m. p. 186°, is obtained by heating 1-*p*-aminophenyl-2-methyl-3-hydroxymethyl-5-pyrazolone with methyl iodide in methyl-alcoholic solution during six to eight hours; it forms colourless crystals, readily soluble in hot, sparingly so in cold water.

The condensation of *p*-nitrophenylhydrazine with ethoxyacetylmalonic ester yields *ethyl* 1-p-*nitrophenyl*-3-*ethoxymethyl* 5-*pyrazolone*-4-*carboxylate*, yellow crystals, m. p. 135—137°, which on heating with hydrochloric acid loses ethyl alcohol and carbon dioxide, giving 1-p-*nitrophenyl*-3-*hydroxymethyl*-5-*pyrazolone*; this on methylation forms 1-p-*nitrophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, and on subsequent reduction yields 1-p-*aminophenyl*-2-*methyl*-3-*hydroxymethyl*-5-*pyrazolone*, m. p. 223—225°.

The condensation of *p*-nitrophenylhydrazine with ethyl acetoacetate gives 1-p-*nitrophenyl*-3-*methyl*-4-*ethyl*-5-*pyrazolone*; this on methylation forms 1-p-*nitrophenyl*-2 : 3-*dimethyl*-4-*ethyl*-5-*pyrazolone*, yellow crystals, m. p. 129—131°, which on bromination yields 1-p-*nitrophenyl*-2-*methyl*-3-*bromomethyl*-4-*ethyl*-5-*pyrazolone*, crystallising in yellow crystals, m. p. 163—165°. The foregoing bromo-compound when heated at 120° in water gives 1-p-*nitrophenyl*-2-*methyl*-3-*hydroxymethyl*-4-*ethyl*-5-

pyrazolone, m. p. 169—170°, which when reduced yields 1-p-*aminophenyl-2-methyl-3-hydroxymethyl-4-ethyl-5-pyrazolone*, a crystalline powder, m. p. 244—245°; this on methylation is converted into 1-p-*dimethylaminophenyl-2-methyl-3-hydroxymethyl-4-ethyl-5-pyrazolone*, m. p. 183—184°. F. M. G. M.

Application of Physico-chemical Methods to Determine the Mechanism of Organic Reactions. ARTHUR MICHAEL (*Amer. Chem. J.*, 1910, **43**, 322—358).—Acree (Abstr., 1907, i, 258), in the course of a study of the behaviour of the metallic salts of tautomeric compounds, discussed the theories advanced by Comstock, Wheeler, Nef and Michael, gave reasons for considering them inadequate to account for the observed reactions, and stated the following generalisation. "A salt of a tautomeric compound reacts with an alkyl halide or other reagent, and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions." He has also stated (Abstr., 1908, i, 920) that when solutions of the salts of 1-phenyl-4-methylurazole are treated with alkyl halides, the latter react with the enolic and ketonic anions of the salts.

In the present paper, these conclusions are criticised at considerable length. It is stated that Acree's interpretations of the mechanism of tautomeric reactions are untenable, and that the results which he obtained in the alkylation of urazole derivatives show that these reactions proceed in accordance with the law of mass action and furnish evidence in support of the "addition theory."

The author protests against theories being put forward with regard to the mechanism of organic reactions which are based on results obtained by physico-chemical methods adapted to the study of dilute solutions of inorganic electrolytes, when the results obtained in other ways and the chemical aspects of the problems are ignored.

E. G.

Urazoles. XV. Reactions of Diazoalkyls with 1-Phenyl-2-methylurazole. SIDNEY NIRDLINGER and SALOMON F. ACREE (*Amer. Chem. J.*, 1910, **43**, 358—384).—In previous papers (Abstr., 1908, i, 919; 1908, ii, 163) the tautomeric behaviour of phenylurazole and its derivatives has been studied with particular reference to the reactions of their metallic salts.

In the present paper, an account is given of the reactions of the urazoles with diazo-derivatives of methane, ethane, propane, butane, and propylene. These substances were selected for study, since they all, except the last, react very rapidly with the urazoles, and yield a mixture of isomeric *O*- and *N*-esters which can be quantitatively separated. It has been found that the equilibrium constants of urazole salts differ from those of the urazoles themselves, but the differences cannot be measured by conductivity methods. A discussion is given of the conditions affecting the constant ratio of products obtained from a tautomeric substance.

1-Phenyl-2-methylurazole, when alkylated with different proportions of diazo-hydrocarbons under similar conditions, yields a constant ratio of esters, thus showing that the constants for the velocity of

rearrangement of the two forms of the compound are very large in comparison with K_{trans} and K'_{trans}, the velocity constants of the reactions of the ketonic and enolic forms respectively with the diazo-compound, or, in other words, that K_3, the equilibrium ratio between the molecular enolic and ketonic forms, is maintained constant during the alkylation. In different solvents, the reaction between 1-phenyl-2-methylurazole and a given diazo-hydrocarbon yields different ratios of the *O*- and *N*-esters; in the same solvent, the urazole and different diazo-compounds give different ratios of esters.

1-Phenyl-2-methylurazole, when treated with diazomethane or diazoethane in presence of its sodium derivative, gives different ratios of esters from those obtained when the sodium salt is absent, and hence the conclusion is drawn that the equilibrium point of the two tautomeric forms of the sodium salt may be different from that of the two forms of the urazole itself, and thus afford an explanation of abnormal hydrolysis.

[With WM. J. HEAPS.]—1-*Phenyl*-2-*methyl*-4-*ethylurazole*, m. p. 112°, obtained by the action of methyl iodide on 1-phenyl-2-methylurazole in presence of potassium hydroxide, evaporating the product to dryness, and treating the residue with hydrochloric acid in order to hydrolyse any *O*-ester present, is a white solid. The corresponding 4-*propyl* and 4-iso*amyl* derivatives have m. p. 75° and 179° respectively; the 4-*butyl* derivative was obtained as a heavy oil.

Propylurethane, b. p. 191·5—192·5°/758 mm., obtained by the action of ethyl chlorocarbonate on propylamine, is a colourless liquid; its *nitroso*-derivative, b. p. 94°(uncorr.)/35 mm., is a red oil. *Butylurethane* has b. p. 208—211°(uncorr.)/770 mm.; its *nitroso*-derivative is a viscous oil. *Allylurethane* has b. p. 194·5—195°(uncorr.)/768 mm.; its *nitroso*-derivative was obtained as a red oil.

1-Phenyl-2-methyl-4-allylurazole, m. p. 61—64°, can be obtained either by the action of diazopropylene on 1-phenyl-2-methylurazole or by the action of allyl iodide on the sodium derivative. E. G.

Condensation of Azoimide with Fulminic Acid. I. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 218—222).—The interaction of azoimide and fulminic acid yields, not triazoformoxime, $N_3\cdot CH:NOH$, but a compound exhibiting all the characters of a 1-hydroxytetrazole. The reaction is probably expressed by the following scheme:

$$C:N\cdot OH + N_3H = N_3\cdot CH:NOH \longrightarrow N\genfrac{}{}{0pt}{}{\diagup N\cdot N\cdot OH}{\diagdown N:CH}$$

(compare Thiele, Abstr., 1892, 1298; Hantzsch and Vagt, Abstr., 1901, i, 194; Forster, Trans., 1909, **95**, 184; Schroeter, Abstr., 1909, i, 773).

1-*Hydroxytetrazole*, CH_2ON_4, forms slender, acicular crystals, m. p. 145° (decomp. with deflagration), and, like most compounds containing the group $:N\cdot OH$ in a heterocyclic chain (compare Peratoner, Abstr., 1902, i, 493), gives with ferric chloride a faint red coloration tending towards brown. The behaviour of 1-hydroxytetrazole towards alkalis corresponds completely with that exhibited by 1-hydroxy-5-phenyltetrazole (compare Forster, *loc. cit.*); gentle heating with 25—30%

alkali solution results in the liberation of one-half of the nitrogen as such, whilst the other half, including the hydroxyiminic nitrogen, is eliminated as ammonia. Similar proportions of nitrogen and ammonia are obtained on heating the compound with concentrated hydrochloric acid in a sealed tube, the hydroxyiminic group here being reduced by the formic acid, which is itself oxidised to carbon dioxide. Among the products of decomposition by concentrated sulphuric acid at a moderately low temperature, hydroxylamine is found.

T. H. P.

Action of Azoimide on Methylcarbylamine: Synthesis of Homologues of Tetrazole. E. OLIVERI-MANDALÀ (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 228—231).—On treating an ethereal solution of anhydrous azoimide with methylcarbylamine, a compound is obtained which gives analytical numbers corresponding with an additive compound of the two substances, but which cannot be regarded as such, as it is not decomposed by prolonged boiling with water, but, like tetrazole, is decomposed completely by alkali into carbon dioxide, methylamine, ammonia, and nitrogen. An additive compound is probably formed first, the reactivity of the triazo-group then causing an immediate intramolecular condensation with formation of the heterocyclic tetrazole ring:

$$N_3\cdot CH{:}NMe \longrightarrow N\Big\langle\begin{matrix}N{:}CH \\ N\cdot NMe\end{matrix}$$

(compare Forster, Trans., 1909, **95**, 184; Schroeter, Abstr., 1909, i, 773).

The *compound*, $C_2H_4N_4$, thus obtained forms hard, elongated prisms with quadrilateral bases, m. p. 36—37°, and exhibits normal cryoscopic behaviour in benzene. Decomposition with boiling concentrated alkali solution takes place according to the equation:

$$C_2H_4N_4 + 2H_2O = N_2 + NH_2Me + NH_3 + CO_2.$$

T. H. P.

Albumin from the Serum of Horse's Blood Deposited on Dialysis into Water. STEPHAN MAXIMOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 330—337. Compare Abstr., 1902, i, 66; 1906, i, 224).—Defibrinated horse's blood was mixed with an equal volume of saturated ammonium sulphate solution and the precipitate filtered, washed with semi-saturated ammonium sulphate solution, dissolved in water, and again precipitated and washed. The precipitate was then dialysed, the solution formed in the dialyser gradually depositing a precipitate as the salts present were removed. This precipitated protein, and that remaining in solution in the dialyser have the following compositions: C, 52·76, 52·61; H, 6·90, 6·83; N, 15·63, 15·53; S, 1·200, 1·211; $[\alpha]_D$ −50·20°, −50·63°. Similar close agreement is observed between the properties of the two derivatives formed with hydrogen chloride. Both parts of this globulin precipitate are therefore apparently identical. Their different behaviour with reference to water is probably due to the presence in the serum of some substance which prevents part of the globulin from

dissolving, and is gradually removed on dialysis, so that the insoluble portion slowly becomes soluble. T. H. P.

The Relations of Proteins to Crystalloids. II. The Osmotic Pressure of Ionising Salts of Serum Proteins. HERBERT E. ROAF (*Quart. J. exp. Physiol.*, 1910, **3**, 171—184. Compare this vol., i, 209).—Observations on amino-acids and proteins confirm the view that these substances form salts with acids and alkali which are ionised, and behave like the salts of fairly strong bases and acids. The formation of such salts is possible in the body, and may explain certain physiological phenomena. W. D. H.

Changes in the Physical Conditions of Colloids. IX. WOLFGANG PAULI and HANS HANDOVSKY (*Biochem. Zeitsch.*, 1910, **24**, 239—262).—Dialysed serum solutions lose, after addition of alkali, their coagulability, which can be restored by addition of salts. The authors have investigated quantitatively the amounts of salts necessary to restore this coagulability in the presence of varying quantities of alkali. They show that the salts of alkaline earths react in this respect more powerfully than those of the alkali metals. They have also determined the coagulation temperatures of the alkaline protein solutions in the presence of various salts, and some of the results are plotted in the form of curves. They have also determined the viscosities and electrical conductivities of some of the mixtures, and have shown that the addition of salts decreases the viscosity of the alkaline protein solution. In these respects, again, the salts of alkaline earths have a more pronounced action than those of the alkali metals. They give formulæ to explain the various phenomena, assuming that on addition of salts the number of hydrated particles of alkali protein is diminished. S. B. S.

Salts of Cytosine, Thymine, and Uracil. VICTOR C. MYERS (*J. Biol. Chem.*, 1910, **7**, 249—258).—The following thymine salts are described: *Sodium*, $C_5H_5O_2N_2Na$, long needles; potassium, $C_5H_5O_2N_2K,\frac{1}{2}H_2O$, small needles; *mercuric*, $C_5H_4O_2N_2Hg$, and *lead*, $C_5H_4O_2N_2Pb,2H_2O$, short needles. Uracil also yields metallic salts; the following have been prepared (compare Johnson and Clapp, Abstr., 1908, i, 836): *Sodium*, $C_4H_3O_2N_2Na,\frac{1}{2}H_2O$; *potassium*,

$$C_4H_3O_2N_2K,H_2O;$$

mercuric, $C_4H_2O_2N_2Hg$, and *lead*, $C_4H_2O_2N_2Pb$.

The sodium salts of both thymine and uracil are convenient for physiological work on account of their solubility, and the comparative insolubility of the two mercuric salts, especially in alkaline solution, can be made use of in precipitating the compounds. The two *silver* salts form gelatinous precipitates which cannot be purified readily.

J. J. S.

The Uric Acid Combinations with Nucleic Acid. ALFRED SCHITTENHELM (*Chem. Zentr.*, 1910, i, 36; from *Zeitsch. expt. Path. Ther.*, 1909, **7**, 110—115).—The compound formed from one molecular equivalent of nucleic acid and two of uric acid, and isolated in the

form of a copper salt by Y. Seo, does not, according to the author, exist, and is only a mixture, the composition of which can be varied by preparing it from varying quantities of the nucleic and uric acids.

S. B. S.

The Presence of Iron in True Nucleic Acids. F. SAUERLAND (*Zeitsch. physiol. Chem.*, 1910, **64**, 16—20).—Nucleic acid from calves' thymus and nucleic acid from herring's spermatozoa contain the merest traces of iron; some samples contain none, others 0·02% to 0·03%. The conclusion is drawn that pure nucleic acid does not contain iron. As most nucleo-proteins contain iron, the question arises as to the part of the molecule in which the iron is to be found. The author suggests that the iron in the nucleo-proteins is due to the presence of impurities. This view is confirmed, as a pancreas nucleo-protein has been obtained practically free from iron (compare Hammarsten, Abstr., 1894, i, 310).

J. J. S.

Formation of Proline by the Hydrolysis of Gelatin with Barium Hydroxide. EMIL FISCHER and REGINALD BOEHNER (*Zeitsch. physiol. Chem.*, 1910, **65**, 118—123).—Proline may either be a primary product of protein hydrolysis or be formed as a secondary product from α-amino-δ-hydroxyvaleric acid (Sörensen, Abstr., 1905, i, 749). Such change is not caused by heating with barium hydroxide. Gelatin, when hydrolysed by barium hydroxide, yields 7·6% proline, a quantity somewhat larger than that hitherto obtained by acid or enzyme hydrolysis (compare Fischer, Levene, and Aders, Abstr., 1902, i, 512). Proline is accordingly a primary product of hydrolysis.

E. F. A.

Filtration of Diastases. MAURICE HOLDERER (*Compt. rend.*, 1910, **150**, 790—792. Compare this vol., i, 212).—Pepsin, emulsin, and the catalase of pork resemble the enzymes already studied in the way in which their filtering power is affected by the alkalinity of the medium. Addition of a neutral salt to a solution of pepsin neutral to methyl-orange restores the power of passing through porcelain. An emulsin prepared from almonds, without employing the usual precipitation by alcohol, was found to pass through filters, whatever the reaction of the solution, provided that the vegetable caseins were first rendered insoluble by treatment with acetic acid. W. O. W.

Chemical Composition and Formation of Enzymes. HANS EULER and BETH AF UGGLAS (*Zeitsch. physiol. Chem.*, 1910, **65**, 124—140).—Portions of invertase solutions were heated for a known time at temperatures above 50° and their hydrolytic activity compared with unheated portions of the same solution. The "inactivity constant" K_E is given by the equation $K_E = 1/t\log.K_0/K$. The temperature-coefficient of this "inactivity constant" rises to a maximum. Invertase is only slightly sensitive to hydrogen ions, but exceedingly sensitive to –OH-ions, and it is compared in this respect with the behaviour of α-glucose on mutarotation. The temperature-coefficient of the hydrolysis of sucrose by invertase is much smaller than that of

the acid hydrolysis. Possibly heating or the presence of hydroxyl ions converts invertase into an inactive form. E. F. A.

Action of Dibasic Alkali Phosphates on Tyrosinase. JULES WOLFF (*Compt. rend.*, 1910, **150**, 477—479. Compare Abstr., 1909, i, 279).—Polemical against Agulhon (Thesis, 1910), who has stated that alkali dibasic phosphates have a retarding influence on the activity of tyrosinase. The author shows by experiments on tyrosine that, taking into consideration the formation of melanins, the extract of *Russula delica* is markedly activated by the addition of disodium phosphate. The melanins obtained in the absence of a phosphate are grey, those precipitated when this is present are deep black. W. O. W.

Halogenated *p*-Aminophenylarsinic Acids. ALFRED BERTHEIM (*Ber.*, 1910, **43**, 529—536).—The arsenic acid group, which is so firmly bound in arsanilic acid and its homologues (Abstr., 1907, i, 812; 1908, i, 591; 1909, i, 75), is very easily eliminated by halogens from *p*-aminophenylarsinic acid, a solution of which in water or aqueous mineral acids yields an almost quantitative amount of tribromoaniline by treatment with bromine water. Mono- and di-halogenated arsanilic acids may be prepared, however, by the action of the halogen in an anhydrous solvent or in *statu nascendi*. Such acids are white, crystalline substances, less basic than arsanilic acid itself, and precipitated from aqueous solutions of their alkali salts by mineral acids. The monohalogenated acids are diazotised easily, the dihalogenated acids with some difficulty, yielding diazo-solutions of remarkable stability.

Bromoarsanilic acid, $NH_2 \cdot C_6H_3Br \cdot AsO(OH)_2$, is best prepared from arsanilic acid and bromine ($\frac{1}{2}$ mol.) in glacial acetic acid. *Iodoarsanilic acid* is prepared by the addition of mercuric oxide and iodine to a hot solution of arsanilic acid in methyl alcohol. *Dichloroarsanilic acid* is obtained by passing chlorine into a suspension of arsanilic acid in glacial acetic acid. *Dibromoarsanilic acid* is prepared by the slow addition of sodium hypobromite to a solution of arsanilic acid in dilute hydrochloric acid at 0°. *Di-iodoarsanilic acid* is obtained by adding arsanilic acid and then a solution of potassium iodide to a hot mixture of potassium iodate and dilute sulphuric acid. None of these acids undergo change below 250°. C. S.

Preparation of Salicylarsinic Acid (6-Hydroxy-1-carboxyphenyl-3-arsinic Acid). WILHELM ADLER (D.R.-P. 215251. Compare Abstr., 1908, i, 591).—The 6-hydroxy-1-carboxyphenyl-3-arsinic acid (salicylarsinic acid) prepared by Kahn and Benda (Abstr., 1909, i, 76) is found to be less toxic than *p*-aminophenylarsinic acid; its *barium* and *silver* salts are colourless, the *copper* salt, greenish-yellow, and the *iron* salt, brownish-red. F. M. G. M.

Isomeric Cinnamic Acids. III. EINAR BIILMANN [and, in part, NIELS BJERRUM] (*Ber.*, 1910, **43**, 568—580. Compare Abstr., 1909, i, 155, 382; this vol., i, 174; Liebermann, Abstr., 1909, i, 303; this vol., i,

36, 175; Stoermer, *ibid.*, i, 115).—The three acids m. p. 42°, 58°, and 68° have practically the same dissociation constants, namely, $K \times 10^6 = 138$, 141, 142. The conclusion is drawn that all three acids yield solutions having the same electrical conductivity (compare Bader, Abstr., 1891, 257), and that the three acids are identical from the chemical point of view.

It has been shown previously (Abstr., 1902, i, 665) that the malenoid forms of olefine compounds containing two negative groups react with mercuric salts, yielding complex mercury compounds. As *allo*cinnamic acid reacts in this manner with mercuric chloride or acetate, whereas ordinary cinnamic does not, the conclusion is drawn that the *allo*-acid has the *cis*-configuration: $\frac{H}{Ph}{>}C\!:\!C{<}\frac{H}{CO_2H}$. The compound obtained is an *inner* salt of *α-mercuri-β-hydroxy-β-phenylpropionic acid*, $OH\cdot CHPh\cdot CH{<}\begin{matrix}CO_2\\ | \\ Hg\end{matrix}$, and is most readily prepared by the addition of a hot solution of mercuric acetate to a hot aqueous solution of *allo*cinnamic acid. It forms a colourless, microcrystalline precipitate with neutral properties, but dissolves in alkali solutions, yielding compounds of the type: $OH\cdot CHPh\cdot CH(Hg\cdot OH)\cdot CO_2Na$. The alkaline solutions are not immediately precipitated by ammonium sulphide, but ultimately yield mercuric sulphide; the solutions react with acids, even carbonic acid, yielding precipitates which are richer in mercury than the original compound. The mercury compound reacts with potassium iodide solution according to the equation:

$$OH\cdot CHPh\cdot CH{<}\begin{matrix}CO_2\\ | \\ Hg\end{matrix} + 2KI + H_2O = OH\cdot CHPh\cdot CH_2\cdot CO_2K + HgI_2 + KOH,$$

and when heated with hydrochloric acid, it yields mercuric chloride and ordinary cinnamic acid. In the latter reaction, β-hydroxy-β-phenylpropionic acid is undoubtedly formed as an intermediate product, but can be isolated more readily by the action of hydrogen sulphide on a solution of the mercury compound in dilute sodium hydroxide.

The complex mercury compounds derived from crotonic and maleic acids (Abstr., 1902, i, 665) are also decomposed by hydrogen sulphide in alkaline solution, yielding respectively β-hydroxybutyric acid and *dl*-malic acid.

The formation of these complex mercury compound appears to be a general method for (*a*) preparing β-hydroxy-acids from certain olefine acids, and (*b*) the elucidation of the *cis*- or *trans*-configuration of olefine acids. J. J. S.

Complex Mercury Compounds of Methyl Cinnamate and Cinnamic Acid. WALTHER SCHRAUTH, WALTER SCHOELLER, and RICHARD STRUENSEE (*Ber.*, 1910, **43**, 695—699. Compare Biilmann, preceding abstract).—When methyl cinnamate is heated with a methyl-alcoholic solution of mercuric acetate at the ordinary temperature, a reaction occurs in which the alcohol participates, and *methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, $OMe\cdot CHPh\cdot CH(CO_2Me)\cdot Hg\cdot OAc$, separates gradually in lance-shaped crystals, m. p. 140·5° (corr.). The

yield amounts to 65%. The acetoxy-group is very reactive, and is replaced by halogen when the substance is treated with halogen salts of sodium. The *chloride* has m. p. 133·5° (corr.); the *bromide*, m. p. 110·5°, and the *iodide*, m. p. 100°. The acetoxy-group is also replaced when the substance reacts with sodium diethylbarbiturate, the corresponding *veronal* derivative being formed. Saponification of methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate yields the internal *anhydride* of *α-hydroxymercuri-β-methoxy-β-phenylpropionic acid*, $CHPh(OMe)\cdot CH<\begin{matrix}CO_2\\ | \\ Hg\end{matrix}$, which decomposes at about 187° (corr.).

Methyl α-acetoxymercuri-β-ethoxy-β-phenylpropionate is prepared by the above method, ethyl alcohol being used instead of methyl alcohol; it has m. p. 123° (corr.). The corresponding *chloride* has m. p. 114°. On saponification the ester yields the internal *anhydride* of the corresponding *acid*. R. V. S.

Action of Dinitrophenylpyridinium Chloride on Mercuriated Amines. FRITZ REITZENSTEIN and GEORG STAMM (*J. pr. Chem.*, 1910, [ii], 81, 150—160).—Mercury derivatives of several compounds have been prepared to ascertain the influence of the metal on colour. *p*-Aminophenyl mercuriacetate reacts with dinitrophenylpyridinium chloride in boiling alcohol to form dinitroaniline and an insoluble, crystalline, brown *substance*, m. p. 244°, which probably has the constitution:

$$C_6H_4<\begin{matrix}N:CH\cdot CH:CH\cdot CH:CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot NH\cdot C_6H_3(NO_2)_2\\ Hg\cdot OAc\end{matrix}$$

(compare Zincke, Abstr., 1904, i, 921). The same two substances react in cold acetone to form an insoluble, brown, crystalline *substance*, $OAc\cdot Hg\cdot C_6H_4\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot OAc$, m. p. 164°. *p*-Aminophenyl mercuriacetate and dinitrophenylpyridinium chloride react in boiling alcohol to form an insoluble, reddish-brown *substance*,

$$HgCl\cdot C_6H_4\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot NH(HCl)\cdot C_6H_4\cdot Hg\cdot OH,$$

m. p. 125°, whilst in cold acetone a reddish-brown *substance*,

$$HgCl\cdot C_6H_4\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot NH(HCl)\cdot C_6H_4\cdot HgCl.$$

m. p. 151°, is produced. The insolubility of these four substances defeats the purpose of their preparation. 3-Mercury-*p*-toluidine, however, when dissolved in pyridine and heated with a methyl-alcoholic solution of dinitrophenylpyridinium chloride yields a brown *substance*, m. p. 133°, $\begin{matrix}CH:CH\cdot NH(HCl)\cdot C_6H_3Me\\ | \\ CH:CH\cdot CH:N\text{——}C_6H_3Me\end{matrix}>Hg$, which is soluble in chloroform. The solution is stated to exhibit faint absorption in the ultraviolet, whilst the analogous non-mercuriated substance prepared by Zincke (*loc. cit.*) shows absorption bands in the yellow and the green. C. S.

Organic Chemistry.

Chemical Effects of Ultraviolet Light on Gases. Polymerising Action. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **150**, 1169—1172).—Exposure of acetylene to the action of ultraviolet light brings about partial polymerisation of the gas, without decomposition and without formation of benzene. The product of polymerisation is a yellow solid, and the residual gas is pure acetylene. Under the same conditions, ethylene polymerises to a liquid having an odour of rancid fat, b. p. below 100°. The product resembles the mixture containing octylene, produced in the pyrogenic decomposition of waxes. Cyanogen is transformed into paracyanogen under the influence of ultraviolet light.

The presence of hydrogen or nitrogen with the acetylene does not modify the action, and mixtures of acetylene with ethylene or cyanogen give simple mixtures of the foregoing products.

W. O. W.

Action of Acetyl Halides on Unsaturated Hydrocarbons in the Presence of Aluminium Halides. S. KRAPIWIN (*Chem. Zentr.*, 1910, i, 1335—1336; from *Bull. Soc. Impér. Natur. Moscou*, 1908, 1).—Unsaturated ketones are obtained by the interaction of acetyl halides, unsaturated hydrocarbons, and aluminium halides, the best results being procured by intimately mixing the reacting substances in a solvent at a low temperature.

*cyclo*Propane (3 mols.), acetyl bromide (3 mols.), and aluminium bromide (4 mols.) in carbon disulphide yield a *ketone*, $C_3H_5 \cdot COMe$, b. p. 103—104°/751 mm., D_4^{19} 0·8548, n_D 1·4253, which forms a *semicarbazone*, m. p. 169·5—170°; by the hydrolysis of the latter, a *ketone*, C_5H_8O, b. p. 96—97°/740 mm., D_4^{25} 0·8585, n_D 1·4240, is regenerated, which shows a marked tendency to polymerise, and forms a *semicarbazone*, m. p. 177—178°. Δ^{δ}-Heptylene, acetyl chloride, and aluminium chloride yield the *ketone*, $C_9H_{16}O$, b. p. 189—190°, D_4^{19} 0·8610, n_D 1·4521 (*semicarbazone*, m. p. 157°). *δ-Hydroxyheptane*, b. p. 154·5°, D_4^{20} 0·8183, n_D 1·4205. *δε-Dibromoheptane*, b. p. 107°/15—17 mm., $D_4^{16\cdot5}$ 1·5250, n_D 1·5035. Δ^{α}-Octene, acetyl chloride, and aluminium chloride yield *Δ^{γ}-decylen-β-one*, $CH_3 \cdot CO \cdot CH:CH \cdot [CH_2]_5 \cdot CH_3$, b. p. 120—122°/38 mm., D_4^{24} 0·8681, n_D 1·4513, in 40% yield, the *semicarbazone* of which has m. p. 149°. Ethylene, acetyl chloride (or bromide), and aluminium chloride (or bromide) in hexane yield *Δ^{α}-buten-γ-one*, $CH_2:CH \cdot COMe$, b. p. 78—80°, D_4^{20} 0·8636, n_D 1·4086, which forms a *semicarbazone*, m. p. 140—141°. By-products of these reactions are halides, $C_nH_{2n+1}X$, and halogen-substituted ketones, $C_nH_{2n}X \cdot COMe$.

C. S.

Action of the Electric Discharge on Chloroform and Carbon Tetrachloride in Presence of Hydrogen, and also on Methyl Chloride. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, **150**, 1118—1121. Compare this vol., ii, 406).—Losanitsch

(this vol., i, 1) has examined the action of the silent electric discharge on chloroform; the present communication describes a repetition of these experiments, in which a mixture of chloroform and hydrogen was employed and a more complete separation of the products effected. The following substances have been recognised in the dark oily mixture obtained: hexachloroethane (the predominating constituent), carbon tetrachloride, pentachloroethane, tetrachloroethylene, hexachloropropylene, heptachloropropylene, and octachlorobutylene. A similar mixture is obtained by the prolonged action of heat. A mixture of carbon tetrachloride with hydrogen gave practically the same products, and, in addition, a compound, $C_4H_2Cl_6$.

Methyl chloride submitted to the discharge in the absence of hydrogen gave a mixture containing dichloroethane, hexachloroethane, tetrachlorobutane, and indefinite fractions varying in composition from $C_3H_5Cl_3$ to $C_4H_5Cl_3$. W. O. W.

Apparatus for Absolute Alcohol. WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1910, **32**, 698—702).—An apparatus is described for the preparation of absolute alcohol in the laboratory. It consists of an outer copper vessel, which serves as a constant-level water-bath, and an inner copper vessel for the alcohol. The latter is provided with a rubber stopper, through which passes a brass tube with two arms, each furnished with a stopcock. One of the arms is connected with a vertical condenser, and the other with a sloping condenser. Quick-lime and alcohol are placed in the inner vessel, and the stopcock is opened in the arm leading to the vertical condenser. The alcohol is boiled until dehydration is complete. The stopcock is then closed, whilst that in the arm leading to the sloping condenser is opened and the alcohol distilled off.

Experiments with this apparatus have shown that it is not possible to remove all the water from alcohol by means of lime, but alcohol of 99·94% strength can be obtained by boiling it for six hours before distilling. If the alcohol is left with the lime at the ordinary temperature for twenty-four hours, it is only necessary to boil it for five hours before distilling. The yield of alcohol can be increased by conducting the dehydration in two stages, and using each time a quantity of lime which is only slightly more than that theoretically required to combine with the water present. In this way, however, the alcohol cannot be obtained so strong as when the dehydration is carried out in one operation in presence of a large excess of lime.

E. G.

Theory of the Formation of Fusel Oil. [Production of Glycerol during Alcoholic Fermentation.] JOSÉ R. CARRACIDO (*Anal. Fis. Quim.*, 1909, **7**, 474—479).—In view of recent papers by Ehrlich (compare Abstr., 1907, ii, 383; 1908, i, 268; ii, 416), in which the formation of fusel oil by the action of yeast on leucine and *iso*leucine is demonstrated, the author refers to his paper (*Revista Acad. Sci. Madrid*, 1904, **1**, 217) dealing with the mechanism of the production of glycerol during alcoholic fermentation. In this paper, which appears to have been overlooked, the formation of glycerol was attributed, not to the decomposition of sugar by the yeast, but to an

autolytic destruction of the yeast itself, probably owing to the action of an enzyme on the protein matter of the yeast cells. This view is strengthened by the fact that when egg-albumin is added to sugar which is undergoing fermentation by yeast, the proportion of glycerol produced is very greatly increased. W. A. D.

Complex Compounds of Glycols. ADOLF GRÜN and E. BOEDECKER (*Ber.*, 1910, **43**, 1051—1062. Compare Grün and Bockisch, Abstr., 1908, i, 932).—The methyl derivatives of glycol give rise to complex metallic compounds in much the same manner as ethylene glycol itself. Some of the compounds are hygroscopic and difficult to isolate. All the compounds examined, including nitrates, chlorides, bromides, and sulphates of cobalt and nickel, contain three molecules of the glycol. They are much less stable than the corresponding metal ammonia salts; their aqueous solutions decompose rapidly, and even the alcoholic solutions are decomposed by alkalis, silver oxide, and sulphides.

Tri-ethylene-glycol-cobaltobromide, $[Co(C_2H_6O_2)_3]Br_2$, obtained by heating hydrated cobalt bromide and ethylene glycol for two hours on the water-bath, crystallises from alcohol in rose-red prisms, and melts at 79° to a deep blue liquid. Its solution in absolute alcohol is blue, and reacts with silver salts, yielding the corresponding chloride and nitrate. When kept over concentrated sulphuric acid, the compound loses ethyleneglycol, and yields *diethylene-glycol-cobaltobromide*

$$CoBr_2,2C_2H_4(OH)_2,$$

as lilac-coloured crystals, m. p. 74°. The *chloride*, $[Co(C_2H_6O_2)_3]Cl_2$, forms blue pyramids, m. p. 68°. It yields a *monohydrate* in the form of rose-coloured crystals, m. p. 63°, and when kept over phosphoric oxide under reduced pressure slowly loses ethylene glycol, yielding *diethylene-glycol-cobaltochloride*, $CoCl_2,2C_2H_6O_2$, as dark lilac-coloured crystals. The *nitrate*, $[Co(C_2H_6O_2)_3](NO_3)_2$, forms deep red crystals, m. p. 52°.

Triethylene-glycol-nickelonitrate, $[Ni(C_2H_6O_2)_3](NO_3)_2$, forms grass-green crystals, m. p. 78°; the *sulphate*, $[Ni(C_2H_6O_2)_3]SO_4,H_2O$, is pale green in colour, and when heated at 100° gives up either 1 molecule of glycol or a molecule of glycol plus water, yielding *diethylene-glycol-nickel sulphate hydrate*, $NiSO_4,2C_2H_6O_2,H_2O$, or the corresponding anhydrous compound, both of which have an apple-green colour.

The complex compounds obtained from glycerol-α-monochlorohydrin do not crystallise; they have been obtained as oils or jellies, except *triglycerol-α-chlorohydrin-nickelochloride*, $[Ni(C_3H_7ClO_2)_3]Cl_2$, which was obtained as green crystals after the lapse of a year.

Tri-glycerol-α-chlorohydrin-chromichloride, $[Cr(C_3H_7ClO_2)_3]Cl_3,3H_2O$, obtained from the two isomeric chromic chloride hexahydrates, forms a syrupy liquid, which appears moss-green in transmitted light, but nearly black in reflected light. The blue chromic chloride yields first a bluish-violet complex salt, but this passes rapidly into the green compound.

Tripropylene-glycol-cobaltochloride, $[Co(C_3H_8O_2)_3]Cl_2$, has a deep blue colour, but turns red on exposure to the air. The corresponding *nitrate* forms a ruby-red, flocculent mass.

Tripropylene-glycol-nickelo-sulphate, $[Ni(C_3H_8O_2)_3]SO_4$, forms a grass-green, vitreous mass.

β-Methylbutylene $\beta\gamma$-glycol yields crystalline, complex salts, but these have not been analysed.

Tripinacone-cobaltonitrate, $[Co(C_6H_{14}O_2)_3](NO_3)_2,2H_2O$, forms well-developed, reddish-violet, monoclinic prisms, m. p. 130°. The *monohydrate* is rose-coloured. The *bromide*, $[Co(C_6H_{14}O_2)_3]Br_2,2H_2O$, forms dark red, crystalline plates, m. p. 136°.

Tripinacone-cobalto-tetrachlorocobaltoate, $[Co(C_6H_{14}O_2)_3]CoCl_4$, obtained by the action of a concentrated solution of cobalt chloride on pinacone hydrate and methyl alcohol, has a deep blue colour when freshly prepared, but becomes sky-blue when exposed to the air or kept over sulphuric acid, owing to the loss of methyl alcohol.

Catechol does not appear to form complex metallic salts (compare Ley and Erler, Abstr., 1908, i, 177). J. J. S.

Glycerolates of the Alkaline-earth Metals. ADOLF GRÜN and J. HUSMANN (*Ber.*, 1910, **43**, 1291—1298).—The hydroxides of calcium, strontium, and barium combine with glycerol, yielding compounds of the type $\left[Ca\vdots\vdots\left(\begin{matrix}OH\cdot CH_2 \\ OH\cdot CH\cdot CH_2\cdot OH\end{matrix}\right)_3\right]OH_2$, in which the glycerol forms a complex radicle with the metallic atom, owing to the subsidiary valencies of two hydroxyl groups of the glycerol. The calcium derivative has been described previously (Grün and Bockisch, Abstr., 1908, i, 935). *Triglycerol barium hydroxide* has been obtained in a crystalline form by dissolving the anhydrous compound in methyl alcohol and adding acetone. It is extremely hygroscopic, and readily absorbs carbon dioxide. The *strontium hydroxide triglycerolate* is similar. *Diglycerol calcium hydroxide hydrate*,

$$Ca(OH)_2,2C_3H_8O_3,H_2O,$$

is formed when calcium hydroxide and water are shaken in the cold with glycerol. It is a yellowish-white, crystalline mass, readily soluble in water, and when heated at 130° loses a molecule of glycerol.

Triglycerol calcium chloride, $[Ca,3C_3H_8O_3]Cl_2$, obtained by dissolving anhydrous calcium chloride in hot glycerol, sets to a vitreous mass, and can be purified by solution in alcohol and precipitation with acetone. The crystalline compound is formed by dissolving hydrated calcium chloride in glycerol and keeping over sulphuric acid. It forms brilliant, transparent cubes, m. p 76°, and is extremely hygroscopic.

Tetraglycerol calcium nitrate, $Ca(NO_3)_2,4C_3H_8O_3$, also forms colourless, transparent crystals, m. p. 72°, but when strongly heated decomposes with explosive violence. The chlorides and nitrates of strontium and barium are not so soluble in glycerol as the calcium salts, and it has not been found possible to prepare crystalline glycerol derivatives. The following products were obtained by adding acetone to the alcoholic solutions: $SrCl_2,7C_3H_8O_3$; $Sr(NO_3)_2,8C_3H_8O_3$, and

$$BaCl_2,7C_3H_8O_3,2H_2O.$$

J. J. S.

Ethyl Ether of Allylcarbinol. H. PARISELLE (*Compt. rend.*, 1910, **150**, 1056—1058. Compare Abstr., 1909, i, 282, 691; Lespieau, Abstr., 1907, i, 580).—The *ether*, $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot OEt$ has been obtained by acting on magnesium allyl bromide with chloromethyl ethyl ether; the compound has b. p. 90°, D^0 0·811, n_D^{17} 1·396, and forms a *dibromo*-derivative, $C_6H_{12}OBr_2$, b. p. 98°/13 mm., D^0 1·76, n_D^{15} 1·512. When the latter is boiled with water, 3-hydroxytetrahydrofuran is formed, together with *αβ-dihydroxy-δ-ethoxybutane*,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot OEt,$$

b. p. 130°/14 mm.; the *diphenylurethane* has m. p. 98—99°.

Hypochlorous acid converts the ether of allylcarbinol into a liquid, b. p. 88—90°/12 mm., consisting of *α-chloro-β-hydroxy-δ-ethoxybutane*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot OEt$, D^0 1·1138, n_D^{17} 1·45, with traces of the ether, $OH\cdot CH_2\cdot CHCl\cdot CH_2\cdot CH_2\cdot OEt$. Hydrogen bromide converts the product into *α-chloro-δ-bromo-β-hydroxybutane*, b. p. 103—106°/13 mm., n_D^{15} 1·52, D^0 1·71. The corresponding epibromohydrin on treatment with potassium hydroxide yields the *ether*, $\overset{CH_2}{\underset{O}{|}}\!\!>CH\cdot CH_2\cdot CH_2\cdot OEt$, b. p. 146—147°.

W. O. W.

Synthesis of the Diprimary Glycols, $HO(CH_2)_{n+2}\cdot OH$, by means of the Dihaloid Compounds, $X(CH_2)_n\cdot X$. R. DIONNEAU (*Bull. Soc. chim.*, 1910, [iv], 7, 327—329).—Hamonet's reaction (Abstr., 1904, i, 401) applied to the dihaloid derivatives of the paraffins furnishes the corresponding alkyl ethers of the glycols, provided that the dihaloid compounds yield true magnesium derivatives of the type $MgBr\cdot[CH_2]_n\cdot MgBr$. The dimethyl ethers of heptamethylene and octamethylene glycols have been prepared in this manner.

α-ε-Dibromopentane dissolves a little less than the quantity of magnesium requisite to form the compound $BrMg\cdot[CH_2]_5\cdot MgBr$, and the liquid reacts with chloromethoxymethane to form αη-dimethoxyheptane, b. p. 104—105°/35 mm. or 201°/760 mm. (compare Abstr., 1907, i, 747).

αζ-Dibromohexane by similar reactions furnishes αθ-dimethoxyoctane, b. p. 121°/35 mm. or 221°/760 mm., and *αθ-diamyloxyoctane*, b. p. 212°/35 mm. Both these ethers furnish with hydrobromic acid the corresponding αθ-dibromo-octane of Solonina (Abstr., 1899, i, 561).

T. A. H.

Synthesis of Ethers of Hexane-αζ-diol: Production of Hexylenic Ethers, $C_6H_{11}\cdot OR$. R. DIONNEAU (*Bull. Soc. chim.*, 1910, [iv], 7, 329—330).—The action of sodium on iodo-ethers (Hamonet, Abstr., 1903, i, 251, 306; Dionneau, Abstr., 1906, i, 134; 1907, i, 747) is more complex than von Braun and Trümpler (this vol., i, 25) suppose, some allyl ether being always formed as well as alkyloxy-derivatives of hexylene in addition to the glycol ethers when alkyloxy-derivatives of iodopropane are used.

Phenoxyhexylene, b. p. 147°/35 mm. or 249°/760 mm., obtained as a by-product in the action of sodium on phenoxyiodopropane, could

not be obtained pure (compare Solonina, Abstr., 1899, i, 561). It combines with one mol. of hydrogen iodide in the cold, forming the *compound*, $OPh\cdot C_6H_{12}I$, b. p. 198°/25 mm., and when warmed with excess of hydriodic acid yields a *di-iodohexane*, b. p. 160°/33 mm., which remains liquid at 0°, and is not identical with $\alpha\zeta$-di-iodohexane. *Methoxyhexylene*, $OMe\cdot C_6H_{11}$, b. p. 123°/760 mm., similarly obtained, gives a *dibromide*, b. p. 148°/30 mm., and *ethoxyhexylene*, b. p. 140°/760 mm., yields a *dibromide*, m. p. 154°/30 mm. T. A. H.

Isomeric Platinum Compounds of Organic Sulphides. LEO TSCHUGAEFF and W. SUBBOTIN (*Ber.*, 1910, 43, 1200—1205).—Compounds of platinous chloride with organic sulphides $PtCl_2,2R_2S$, exist in two modifications; in the case of $PtCl_2,2Me_2S$, a third insoluble, red-coloured isomeride, the γ-salt, has been described. Various formulæ have been ascribed to this isomeride; both Blomstrand (Abstr., 1889, 230) and Klason (Abstr., 1895, i, 488) considered the possibility of it being an analogue of the green Magnus salt, and having the formula $[Pt4Me_2S]PtCl_4$, but abandoned this constitution.

It is now shown that on shaking the red γ-salt in aqueous solution with Reiset's chloride, $(Pt4NH_3)Cl_2$, it becomes green, and is converted into the Magnus salt, $[Pt4NH_3]PtCl_4$. Accordingly, the above constitution is established for the red γ-salt. The two other isomerides derived from methyl sulphide do not interact with Reiset's chloride.

Similar compounds are formed by platinum chloride and 1 : 2-dithioglycol ethers. Thus, ethylene dithioglycol ether when shaken with potassium platinichloride in cold aqueous solution forms small, flesh-coloured prisms or needles of the compound $PtCl_2,C_2H_4(SEt)_2$. When shaken with the Reiset's salt, the red isomeride is converted into the green Magnus salt. When the red compound is warmed with water, it is slowly converted into a yellow isomeride; the same change takes place more quickly in the dry state at 136·5°. The yellow isomeride has m. p. 188°, and does not react with Reiset's salt. It is formed directly when potassium platinichloride and disulphide interact at 100°.

Similarly, *n*-propyl 1 : 2-dithioglycol ether reacts with potassium platinichloride, forming a red substance, which is transformed into a yellow isomeride at higher temperatures, and yields Magnus salt with Reiset's chloride. In this case the Magnus salt is first obtained in a red modification, which slowly, or more quickly on heating, changes into the normal green form. E. F. A.

Glucinum Formates. SEBASTIAN M. TANATAR (*Ber.*, 1910, 43, 1230—1231).—Normal glucinum formate, $Gl(CHO_2)_2$, may be obtained by the solution of glucinum carbonate in 50 or 90% formic acid and evaporation of the solution at 100—110°, or in a desiccator. This is in contradistinction to the indirect methods which have to be used to prepare the normal acetate and propionate (compare Abstr., 1907, i, 888).

Glucinum formate is insoluble in organic solvents. The aqueous solution undergoes hydrolysis only after prolonged boiling, the resulting

basic salt having a composition intermediate between $Gl(CHO_2)_2$ and $Gl_4O(CHO_2)_6$. On heating under diminished pressure (30—35 mm.), the normal salt gives a sublimate of the basic salt, $Gl_4O(CHO_2)_6$.

T. S. P.

Ethyl Acetate. ALEX. BOGOJAWLENSKI and J. NARBUTT (*J. pr. Chem.*, 1910, [ii], **81**, 420—421).—The preparation of ethyl acetate by the aid of anhydrous copper sulphate (Habermann and Brezina, Abstr., 1909, i, 873) has been described by the authors (Abstr., 1905, i, 854).

C. S.

Solidification of Binary Mixtures of the Saturated Monobasic Fatty Acids and Water. REZSÖ BALLÓ (*Zeitsch. physikal. Chem.*, 1910, **72**, 439—450).—The fact that formic and acetic acids produce abnormally small depressions of the freezing point of water has been ascribed by previous observers to association of the acids, but the author now shows that it is due to the formation of solid solutions of water and the respective acids.

The mixtures of acid and water were partly frozen, the mother liquor removed by filtration and centrifugal action, portions of the solid mass melted, and the liquid removed in order to secure as complete a separation of the mother liquor as possible; the crystals were then analysed. In spite of these precautions, evidence was obtained that the separation from the mother liquor was by no means complete, so that the results are only qualitative.

Acetic acid and water form four series of mixed crystals, which separate from solutions containing 0—40%, 40—59%, 59—77%, and 77—100% by weight of the acid respectively. The results with the other acids are similar, except that propionic acid appears to form a definite compound with water of the formula $H_2O,11C_2H_5\cdot CO_2H$. The eutectic temperature of mixtures of butyric acid and water is $-10\cdot4°$; the eutectic mixture contains 88·91% by weight of the acid. G. S.

Essence of Cocoanut Butter. Composition of Cocoanut Oil. ALBIN HALLER and A. LASSIEUR (*Compt. rend.*, 1910, **150**, 1013—1019).—Commercial cocoanut oil owes its unpleasant odour to the presence of hexoic, octoic, and decoic acids arising from hydrolysis of the glycerides, and also to certain neutral compounds, chiefly methyl heptyl ketone and methyl nonyl ketone. The presence of a small quantity of an optically active aldehyde has also been recognised. The odorous substances may be separated by distillation in superheated steam, and constitute the mixture known as essence ("échappées") of cocoanut butter. The ketones appear to exist in the butter, and not to be formed during distillation.

When methyl nonyl ketone is hydrogenated in presence of reduced nickel at 250—300°, it yields a *hydrocarbon*, C_9H_{20}, b. p. 150—155°/760 mm., and a *pinacolin*, m. p. 27°, to which the constitution

$$C_9H_{19}\cdot CMe_2\cdot CO\cdot C_9H_{19}$$

is ascribed; this substance is unaltered by alkaline hypobromite, but forms an *oxime*, b. p. 233—237°, and a *semicarbazone*, m. p. 225—227°.

W. O. W.

Syntheses of Symmetrical Monoglycerides. ADOLF GRÜN (*Ber.*, 1910, **43**, 1288—1291).—α-Monoglycerides,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot COR,$$

have been synthesised already by Krafft (Abstr., 1904, i, 137) and Guth (Abstr., 1903, i, 225). The author has prepared a number of β-monoglycerides, $COR\cdot O\cdot CH(CH_2\cdot OH)_2$, by the action of β-monochlorohydrin on the salts of fatty acids. The same glycerides have also been prepared more conveniently from the αγ-dichlorohydrin: first converting it into the compound $COR\cdot O\cdot CH(CH_2Cl)_2$ by the action of an acyl chloride, and then replacing the two chlorine atoms by hydroxyl through the agency of silver nitrite (compare Grün and Theimer, Abstr., 1907, i, 464).

β-Lauryl αγ dichlorohydrin, $C_{11}H_{23}\cdot CO\cdot O\cdot CH(CH_2Cl)_2$, forms a yellow, mobile oil, and when heated with its own weight of silver nitrate in a stream of hydrogen at 120°, yields *β-monolaurin*,

$$C_{11}H_{23}\cdot CO\cdot O\cdot CH(CH_2\cdot OH)_2,$$

which crystallises in glistening needles, m. p. 61°, after sintering at 58°. When kept for some time, it has m. p. 57·5°. *β-Monopalmitin*, $C_{15}H_{31}\cdot CO\cdot O\cdot CH(CH_2\cdot OH)_2$, crystallises in plates, m. p. 74°, but after several months the m. p. is 69·5°. J. J. S.

Partial Hydrogenation of Acids in the Stearolic Series and Isomerism of their Hydriodo-derivatives. ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1910, **150**, 1130—1132).—Holt (Abstr., 1892, 962) has stated that behenolic acid is reduced by zinc dust and acetic acid to brassidic acid; this author's experiments have now been repeated, but without success. Reduction, however, was accomplished by passing hydrogen iodide into the fused acid and heating the resulting iodo-derivative with zinc dust and acetic acid for twelve to twenty-four hours. Other stearolic acids have been reduced in the same way: thus tariric acid yields *Δζ-elaidic acid*, $C_{18}H_{34}O_2$, for which the name *tarelaidic acid* is suggested; it crystallises in prisms, m. p. 52·5°, and on oxidation furnishes cis-*ζη-dihydroxystearic acid*, $C_{18}H_{36}O_4$, m. p. 117·5°.

The addition of hydrogen iodide to stearolic acids appears to take place in such a way that two isomeric derivatives of the types $CIR\colon CHR'$ and $CHR\colon CIR'$ are formed. The separation of the two isomerides produced in this way from stearolic and behenolic acids is described. The iodoelaidic acids have m. p. 39° and 23—24°, whilst the corresponding derivatives of brassidic acid have m. p. 48° and 37—38° respectively. W. O. W.

Condensation of Secondary Amines with Ethyl γ-Bromo-αα-dimethylacetoacetate. HENRI GAULT and G. THIRODE (*Compt. rend.*, 1910, **150**, 1123—1125).—*Ethyl γ-diethylamino-αα-dimethylacetoacetate*, $NEt_2\cdot CH_2\cdot CO\cdot CMe_2\cdot CO_2Et$, b. p. 118°/14 mm., has been prepared by adding diethylamine (2 mols.) to ethyl γ-bromo-αα-dimethylacetoacetate in dry ether (Conrad, Abstr., 1897, i, 321; 1899, i, 193). The substance has not yielded crystalline derivatives, and undergoes decomposition when heated with phenylhydrazine; on hydrolysis with dilute acids, it furnishes *diethylaminomethyl isopropyl*

ketone, $NEt_2 \cdot CH_2 \cdot COPr^{\beta}$, b. p. 75°/14 mm., 182° under atmospheric pressure.

Ethyl γ-ethylanilino-aa-dimethylacetoacetate,
$$NEtPh \cdot CH_2 \cdot CO \cdot CMe_2 \cdot CO_2Et,$$
b. p. 189°/13 mm., furnishes a *3-ethylanilinomethyl-1-phenyl-4 : 4-dimethylpyrazolone*, m. p. 77°, and gives on hydrolysis *ethyl anilinomethyl isopropyl ketone*, $NEtPh \cdot CH_2 \cdot COPr^{\beta}$, a colourless liquid, b. p. 154°/14 mm., becoming yellow on exposure to light; the unstable *phenylhydrazone* has m. p. 87°. W. O. W.

Velocity of Electrolytic Oxidation of Certain Organic Acids. F. AGENO and G. DONINI (*Gazzetta*, 1910, 40, i, 21—31).—The authors discuss previous investigations on the velocity of reaction in electrochemical processes, more especially reduction processes. In their own experiments on the electrolytic oxidation of organic acids, an apparatus was employed similar to that used by Åkerberg (Abstr., 1902, ii, 488), the cathode of smooth platinum being surrounded by a small glass bell in order to allow the hydrogen liberated to escape without coming into contact with the anode, which was composed of a peroxide. In the case of oxalic acid, with an anode of lead peroxide, the unimolecular reaction constant gradually increases, whilst the values of Goldschmidt's constant, $K_1 = 3(\sqrt[3]{a} - \sqrt[3]{a-x})/t_1$ (*Zeitsch. Elektrochem.*, 1900, 7, 263), remain moderately constant. The velocity of reaction is hence proportional to $C^{\frac{2}{3}}$, which expresses the concentration in a section, so that the reaction takes place at the surface of the electrode. From the beginning the action consists of an oxidation due to the oxygen evolved, the anode acting as a catalyst; this behaviour is in complete agreement with the observation that the oxidation of oxalic acid by lead peroxide proceeds spontaneously at the ordinary temperature, and with the course of the anode-potential, which, apart from an initial depolarising action on the electrode, remains constant. With sodium hydrogen oxalate, the velocity-constants are considerably less than with oxalic acid, so that it appears probable that the non-dissociated acid and the ion HC_2O_4 are preferably oxidised, this confirming the hypothesis that the oxidation is a secondary phenomenon of a chemical nature occurring under the specific catalytic influence of the electrode.

With an anode of manganese dioxide, the velocity of oxidation and the course followed by the anode-potential are perfectly analogous to those obtained with lead peroxide. When an anode of nickel or cobalt peroxide is employed in a solution rendered alkaline by sodium hydroxide, no oxidation of oxalic acid takes place, the C_2O_4 ion remaining unattacked by the oxygen developed electrolytically.

Malonic and succinic acids are not altered by the anodic oxygen liberated at an anode of platinised platinum or of lead or manganese dioxide, but the alkali salts of these acids undergo oxidation (compare Petersen, Abstr., 1898, i, 352). For the oxidation of the potassium salts at an electrode of lead peroxide, neither the formula for a unimolecular reaction nor Goldschmidt's formula gives a constant value for the reaction constant, several reactions apparently occurring simultaneously at the electrode. T. H. P.

Hydrazine Oxalates. J. W. TURRENTINE (*J. Amer. Chem Soc.*, 1910, **32**, 577—588).—Two *oxalates* of hydrazine, $2N_2H_4,H_2C_2O_4$ and $N_2H_4,H_2C_2O_4$, are described. The former crystallises in needles and plates, and is soluble to the extent of 2·009 grams in 1 gram of water at 35°. When heated in a capillary tube, it begins to decompose at 130°, and afterwards melts to a clear liquid, which solidifies on cooling with production of a substance of m. p. about 150°. The decomposition of the salt by heat has been studied under various conditions, and it has been found that the decomposition products are water, ammonia, hydrogen cyanide, hydrazine, carbon dioxide and monoxide, nitrogen, and carbon. A complex hydrazine *compound* is also formed as a white, crystalline sublimate.

The other salt, $N_2H_4,H_2C_2O_4$, forms lustrous, monoclinic needles [$\beta = 63°20'$], and is soluble only to the extent of 0·0204 gram in 1 gram of water at 22·5°, but is readily soluble in boiling water. When heated in a capillary tube at 200°, it is converted into a liquid which does not solidify on cooling. On destructive distillation, it yields water, ammonia, hydrogen cyanide, carbon dioxide and monoxide, nitrogen, and carbon, together with a white sublimate which appears to be an ammonium compound. If the decomposition is effected in a sealed tube, a substance is obtained which is probably a hydrazine salt of an acid containing carbon. When this oxalate is dissolved in water, one-half of the acid is liberated and can be titrated with alkali. E. G.

Compounds with a Branched Chain. III. Mlle. GERMAINE FREYLON (*Ann. Chim. Phys.*, 1910, [viii], **20**, 58—115. Compare this vol., i, 296)—The author describes the preparation of compounds with highly branched chains, and points out the influence of such chains in modifying the general properties of these substances.

The following derivatives of *iso*butylmalonic acid are mentioned: the *dimethyl* ester, b. p. 101°/15 mm.; *diethyl* ester, b. p. 119—120°/16 mm.; the *dichloride*, b. p. 83—85°/22 mm.; the *diamide*, needles, m. p. 195—196°.

Di*iso*butylmalonic acid has m. p. 157—158°; Perkin and Bentley (Trans., 1898, **73**, 61) give 145—150°, but their preparation probably contained some *monomethyl* ester, b. p. 155—160°/12 mm. The *methyl ethyl* ester has b. p. 140—142°/18 mm.; the diethyl ester, b. p. 148—150°/14 mm.; the *dichloride*, b. p. 136—140°/20 mm.; the *diamide* forms pearly leaflets, m. p. 280—281°. γ-Methyl-α-*iso*butylvaleric acid, obtained by heating the foregoing acid, has b. p. 139—141°/18 mm., D_0^4 0·913 (compare Perkin and Bentley, *loc. cit.*); the *methyl* ester has b. p. 87—89°/15 mm.; the *ethyl* ester, b. p. 91—93°/13 mm., D_0^4 0 870; the *ketonic* ester,

$$(C_4H_9)_2CH\cdot CO_2\cdot CH_2\cdot COMe,$$

b. p. 135—140°/13 mm, forms a *semicarbazone*, m. p. 119—120° (compare Locquin, Abstr., 1904, i. 644). The corresponding *ketonic* ester of γ-methylvaleric acid, $CH_2Pr^{\beta}\cdot CH_2\cdot CO_2\cdot CH_2\cdot COMe$, forms a *semicarbazone*, m. p. 70—71°.

γ-Methyl-α-*iso*butylvaleric acid has also been characterised by means of the *chloride*, b. p. 80—83°/13 mm., and the *amide*, which crystallises in lamellæ, m. p. 74—75°; the substance described by Perkin and Bentley under this name is shown to be γ-methylvaleramide. When the acid chloride is treated successively with bromine and alcohol, *ethyl* α-*bromo*-γ-*methyl*-α-iso*butylvalerate*,

$$CBr(CH_2Pr^\beta)_2\cdot CO_2Et,$$

b. p. 130—135°/14 mm., is obtained; the corresponding *bromoamide* has m. p. 77—78°, and yields di*iso*butyl ketone when treated according to the method of Mannich and Zernich (Abstr., 1908, i, 399).

Ethyl γ-methyl-α-*iso*butylvalerate, on reduction with sodium and alcohol, forms δ-methyl-β-*iso*butylpentanol, the *pyruvate* of which has b. p. 135—140°/21 mm., and gives a *semicarbazone*, m. p. 159—160°; the *phenylurethane* has m. p. 54—55°.

The reduction of ethyl di*iso*butylmalonate leads to the formation of the foregoing pentanol, together with di*iso*butyltrimethylene glycol and γ-*methyl*-α-*hydroxymethyl*-α-iso*butylvaleric acid*,

$$OH\cdot CH_2\cdot C(CH_2\cdot CHMe_2)_2\cdot CO_2H,$$

m. p. 83—84°. The *methyl* ester of this compound has b. p. 121—123°/11 mm., D_0^4 0·973; the *ethyl* ester, b. p. 133—135°/15 mm., was prepared by the action of formaldehyde on α-bromo-γ-methyl-α-*iso*butylvalerate in presence of magnesium amalgam; at the same time there is formed *ethyl* $\beta\beta\delta\delta$-*tetra*iso*butylacetoacetate*,

$$CH(CH_2Pr^\beta)_2\cdot CO\cdot C(CH_2Pr^\beta)_2\cdot CO_2Et,$$

m. p. 59—60°, a very stable substance which has not yet been hydrolysed.

The application of Grignard's reaction to ethyl γ-methyl-α-*iso*butylvalerate results in the formation of $\beta\epsilon$-*dimethyl*-γ-iso*butylhexan*-β-*ol*, $CH(CH_2Pr^\beta)_2\cdot CMe_2\cdot OH$, b. p. 93—94°/7 mm.; pyruvic acid converts this into $\beta\epsilon$-*dimethyl*-γ-iso*butyl*-Δ^β-*hexene*, b. p. 65°/10 mm.; the corresponding *diphenylurethane* has b. p. 240°. Magnesium methyl iodide acts on ethyl di*iso*butylmalonate, forming γ-*methyl*-α-*hydroxy*-iso*propyl*-α-iso*butylvaleric acid*, $OH\cdot CMe_2\cdot C(C_4H_9)_2\cdot CO_2H$, b. p. 155—160°/15 mm., and ϵ-*methyl*-γ-iso*butylhexan*-β-*one*,

$$(CH_2Pr^\beta)_2CH\cdot COMe,$$

b. p. 82—84°/12 mm. The synthesis of this ketone has been effected by three other methods, and its constitution determined from a study of its oxidation products; the *semicarbazone* has m. p. 138—139°, the *oxime*, b. p. 123—126°/10 mm.

By dehydrogenating δ-methyl-β-*iso*butylpentanol in presence of reduced copper, α-*iso*butyl*iso*hexoaldehyde, $CH(CH_2Pr^\beta)_2\cdot CHO$ (Behal and Sommelet, Abstr., 1904, 222), has been obtained, accompanied by a bimolecular polymeride. The aldehyde has b. p. 82—83°/18 mm., D_0^4 0·825, and forms an *oxime*, b. p. 125—126°/20 mm., and a *semicarbazone*, m. p. 139—140°, identical with that obtained from the polymeride, $C_{20}H_{40}O_2$, b. p. 160—170°/20 mm. W. O. W.

Dibromomaleic Anhydride. I. OTTO DIELS and MARTIN REINBECK (*Ber.*, 1910, **43**, 1271—1279).—Attempts have been made to

eliminate bromine from dibromomaleic anhydride and iodine from di-iodomaleic anhydride, but without success.

Ethyl malonate readily combines with the dibromo-anhydride, yielding a diethyl ester of *aβ-dibromo-Δ^a^-butylene-γ-one-aδδ-tricarboxylic acid*, $CO_2H\cdot CBr\colon CBr\cdot CO\cdot CH(CO_2Et)_2$, which is readily hydrolysed to dibromomaleic acid and ethyl malonate, but when heated at 100° with glacial acetic acid saturated at 0° with hydrogen bromide, it yields 4 : 5-dibromo*cyclo*pentene-1 : 3-dione, $CH_2<\begin{matrix}CO\cdot CBr\\ \|\\ CO\cdot CBr\end{matrix}$, the parent substance of Wolff and Rüdel's tribromo*cyclo*pentenedione (Abstr., 1897, i, 215).

A good yield of dibromomaleic acid can be obtained by oxidising mucobromic acid at low temperatures (25—30°) with an amount of nitric acid (D 1·5) necessary for solution (compare Hendrixson. Abstr., 1890, 958). The acid has m. p. 142°, the m. p.'s previously given, namely, 120° to 125°, are low, owing to the presence of small amounts of anhydride.

Di-iodomaleic anhydride, $C_4O_3I_2$, obtained by the action of sodium iodide on an acetone solution of the dibromo-anhydride, crystallises in glistening, yellow needles, m. p. 116°.

Methyl hydrogen dibromomaleate, $CO_2H\cdot CBr\colon CBr\cdot CO_2Me$, prepared by the action of methyl alcohol on the anhydride, crystallises in long slender needles, m. p. 78—79°.

Diethyl hydrogen aβ-dibromo-Δ^a^-butylene-γ-one-aδδ-tricarboxylate,

$$CO_2H\cdot CBr\colon CBr\cdot CO\cdot CH(CO_2Et)_2,$$

crystallises in small, rhombic plates, m. p. 76—77°, and yields a *potassium* salt, which also crystallises in plates.

4 : 5-*Dibromo*cyclo*pentene*-1 : 3-*dione*, $C_5H_2O_2Br_2$, crystallises in pale yellow, nacreous plates, m. p. 157—158°, and reacts with a chloroform solution of bromine at the ordinary temperature, yielding 2 : 2 : 4 : 5-*tetrabromo*cyclo*pentene*-1 : 3-*dione*, $CBr_2<\begin{matrix}CO\cdot CBr\\ \|\\ CO\cdot CBr\end{matrix}$, which crystallises in yellow needles, m. p. 140—143°.

Dimethyldibromomaleide, $O<\begin{matrix}CMe_2\cdot CBr\\ \|\\ CO—CBr\end{matrix}$, obtained by the action of magnesium methyl iodide on an ethereal solution of dibromomaleic anhydride and subsequent treatment with dilute sulphuric acid, crystallises in compact prisms, m. p. 129—130°. J. J. S.

Inertia of Crystallisation of Tartrate Mother Liquors. P. CARLES (*Bull. Soc. chim.*, 1910, [iv], 7, 326—327).—Calcium tartrate of commerce, containing iron, is often difficult to use as a source of tartaric acid, since on addition of sulphuric acid complex iron compounds are formed, which inhibit crystallisation of the tartaric acid. These may be eliminated by adding enough potassium ferrocyanide to precipitate all the iron. The filtrate from the precipitated Prussian-blue then usually deposits crystals of tartaric acid on evaporation. A little hydrocyanic acid is evolved in the reaction, so that the operation should be conducted in the open air.

T. A. H.

Interchange of Alkyl Groups in Acid Esters. TELEMACHOS KOMNENOS (*Monatsh.*, 1910, **31**, 111—122).—By the interaction of sodium ethoxide, ethyl malonate and iodine, ethyl ethanetetracarboxylate, m. p. 77°, is formed. When sodium methoxide was substituted for the ethoxide, colourless, glistening crystals, m. p. 135°, were obtained, together with a viscid oil. The crystals proved to be tetramethyl ethanetetracarboxylate (compare Walker, Trans., 1895, **67**, 770), which may also be obtained by the action of sodium methoxide on ethyl ethanetetracarboxylate, and, alternatively, the methyl ester is converted by sodium ethoxide into the ethyl ester. E. F. A.

Ester Acids of Thiocarboxylic Acids with Aliphatic Alcohol Acids. IV. Preparation of Rhodanins. BROR HOLMBERG (*J. pr. Chem.*, 1910, [ii], **81**, 451—465. Compare Abstr., 1909, i, 286).—Two methods for the preparation of rhodanins are described. In one a dithiocarbamate is treated with an aqueous solution of an alkali salt of a halogen-substituted acid, and the solution of the resulting substituted dithiocarbamate is acidified by acetic acid, whereby the rhodanin is slowly precipitated (*loc. cit.*). The second method, which is more elegant but less widely applicable, depends on the fact that hot aqueous solutions of the trithiocarbodiglycollates of certain primary amines decompose into thioglycollic acid and thiocarbamylthioglycollic acids, the latter of which yield rhodanins: $CS(S{\cdot}CH_2{\cdot}CO_2H)_2 + R{\cdot}NH_2 \longrightarrow SH{\cdot}CH_2{\cdot}CO_2H +$

$$NHR{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H \longrightarrow S{<}\begin{matrix}CH_2{\cdot}CO\\ |\\ CS{-}NR\end{matrix}.$$

In addition to β-methylrhodanin, *N*-ethylrhodanin, *N*-phenylrhodanin, *N*-benzylrhodanin, *N*-*o*-tolylrhodanin, the corresponding *m*- and *p*-isomerides, *N*-phenyl-β-methylrhodanin, *N*-aminorhodanin, and *N*-anilinorhodanin, the following new compounds have been prepared (by the second method): N-o-*Methoxyphenylrhodanin*, $OMe{\cdot}C_6H_4{\cdot}N{<}\begin{matrix}CS{-}S\\ |\\ CO{\cdot}CH_2\end{matrix}$, m. p. 142·5—143°, and the para-*isomeride*, m. p. 155·5—156°, from *o*- and *p*-anisidine respectively, and N-p-*bromophenylrhodanin*, m. p. 164—165°, from *p*-bromoaniline; α- and β-naphthylamines yield only the corresponding dinaphthylthiocarbamides. C. S.

Glutardialdehyde. CARL D. HARRIES (*Ber.*, 1910, **43**, 1194. Compare Abstr., 1908, i, 517).—The dioxime of this substance forms long, white needles, m. p. 171°. The m. p. of the nitrophenylhydrazone formerly described can be raised by recrystallisation from toluene to 160—161°. R. V. S.

Tautomerism of Aliphatic Ketones. V. H. HÂNCU (*Ber.*, 1910, **43**, 1193).—Polemical. A reply to Ostrogovich (Abstr., 1909, i, 764). The figures criticised by the latter were not the actual experimental results; these are now quoted, and are in agreement with the theoretical values. R. V. S.

Thalloacetylacetone. EDUARD KUROWSKI (*Ber.*, 1910, **43**, 1078—1079).—Thalloacetylacetone, prepared by boiling thallium

carbonate with acetylacetone in alcoholic solution, crystallises in colourless, flat needles, which are transparent in ordinary light, and show a marked interference coloration in polarised light; m. p. 160° (decomp.). Very characteristic is the formation of a voluminous, orange precipitate with a few drops of carbon disulphide in alcohol or benzene solution; this affords a very delicate test for carbon disulphide, and similar, although differently coloured, precipitates are obtained with other organic sulphur compounds. E. F. A.

Condensation of Pinacolin with Esters. FRANÇOIS COUTURIER (*Compt. rend.*, 1910, **150**, 928—930. Compare Abstr., 1905, i, 570).—Further proof of the ketonic character of pinacolin is afforded by the fact that this substance undergoes condensation with esters in presence of sodium or sodium ethoxide, giving compounds having all the characteristics of β-diketones, and yielding *iso*oxazoles with hydroxylamine.

ββ-Dimethylhexan-γε-dione, $CMe_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$, prepared from pinacolin and ethyl acetate, has b. p. 168°, D^0 0·933, and develops an intense red coloration with ferric chloride. The *sodium* and *copper* salts are crystalline, the latter having m. p. 175°; *5-methyl-3-*tert.*-butyl*iso*oxazole*, $C_8H_{13}ON$, has m. p. 107°, the *phenylhydrazone*, m. p. 85°.

Ethyl trimethylacetylpyruvate, $CMe_3\cdot CO\cdot CH{:}C(OH)\cdot CO_2Et$, obtained from ethyl oxalate, has b. p. 124°/13 mm., and forms a *copper* salt crystallising in deep green prisms, m. p. 162°; *ethyl 3-*tert.*-butyl*iso*oxazole-5-carboxylate* forms needles, m. p. 90°. The ester is soluble in sodium carbonate solution, from which it is precipitated by acids; hydrolysis in cold alkaline solution leads to the production of *trimethylacetylpyruvic acid*, $C_8H_{12}O_4$, m. p. 60°. No evidence has been obtained of the existence of this compound or its ester in the ketonic form. W. O. W.

New Synthetical Passage from the Aliphatic to the Aromatic Series. TELEMACHOS KOMNENOS (*Monatsh.*, 1910, **31**, 135—141).—By the condensation of tetra-acetylethane with succinic acid and acetic anhydride, a compound, $C_{14}H_{16}O_6$, is formed, which has a characteristic aromatic odour and crystallises in large needles, m. p. 60°. It is not an acid, but is unsaturated, forming a bromine additive product, m. p. 72°, from which hydrogen bromide is easily eliminated. Dilute nitric acid oxidises it, yielding oxalic acid. It contains acetyl groups, and after hydrolysis yields a compound, m. p. 178°.

E. F. A.

Lactose and its Behaviour in Aqueous Solutions. WILHELM FLEISCHMANN and G. WIEGNER (*J. Landw.*, 1910, **58**, 45—64).—The sp. gr. values obtained by Schmoeger for solutions of lactose up to 36% and those given in the present paper for greater concentrations may be calculated as functions of the concentration x in weights per cent. by the following formula: $D_4^{20} = 0{\cdot}9982 + 3{\cdot}7585x.10^{-3} + 1{\cdot}1284x^2.10^{-5} + 5{\cdot}8405x^3.10^{-8}$.

The formula gives values for D up to 62·05% of crystallised lactose. With concentrations of 11·96%, the D is correctly given by the first three members of the equation.

The probable value for D of pure liquid lactose is $D_4^{20} = 1{\cdot}5453$. When lactose is dissolved in water, a contraction, varying with the

concentration, takes place, being greatest in solutions containing 54·03%, in which the contraction amounts to 0·596 c.c. in 100 grams of solution.

Assuming other constituents of milk to have no effect, the contraction in 100 grams of average milk, due to lactose, will be 0·094 c.c., and will vary between 0·077 and 0·116 c.c.

The results of calculations of the volume of milk from the sum of the volumes of the single constituents make it probable that the sp. gr. of liquid proteins is about D_{15}^{15} 1·46. N. H. J. M.

Some Kinds of Gums. Ernst Meininger (*Arch. Pharm.*, 1910, **248**, 171—201).—Gums obtained from various species of Acacia grown in known localities have been examined. The gum from *Acacia pycnantha*, grown in Victoria and South Australia, contains 13·55% of moisture, 0·92% ash (0·28% being calcium and 0·123% magnesium), 0·64% of matter insoluble in water; the aqueous solution has an acid reaction, does not reduce Fehling's solution, and has α_D −19·39° ($p=7·9992$ and $D=1·0325$). The arabic acid, that is, the organic part remaining after the removal of the inorganic constituents, contains 1·31% of nitrogen, whereas the unpurified dried gum contains 2·19%. The dried gum yields a yellow, amorphous *acetyl* derivative by treatment with acetic anhydride and sodium acetate at 110—120°. By oxidation with nitric acid, D 1·15, the gum yields an amount of mucic acid corresponding with 58·61% of galactan, whilst the furfuraldehyde and methylfurfuraldehyde obtained by distilling the gum with 12% hydrochloric acid represent 16·98% of pentosan and 2·92% of methylpentosan respectively. Hydrolysis of the gum by dilute sulphuric acid yields *d*-galactose and *l*-arabinose.

The gum from *Acacia horrida*, grown in South and South-West Africa, contains moisture 15·34%, ash 2·59% (Ca 1·06%; Mg 0·345%), matter insoluble in water 0·98%. Its aqueous solution has α_D 53·94° ($p=8·156$; $D=1·0342$). The acetylated gum is a light brown powder. The arabic acid contains 0·71% of nitrogen, whilst the original gum contains 1·51%. The mucic acid obtained by oxidation represents 27·36% of galactan; the amounts of pentosan and methylpentosan are 36·50 and 2·82% respectively. Hydrolysis of the gum by dilute sulphuric acid yields *l*-arabinose and *d*-galactose.

The gum (Babool gum) from *Acacia arabica,* grown in Africa, Arabia, and India, contains moisture 14·39%, ash 2·41% (Ca 0·765%; Mg 0·106%), and is only partly soluble in water. It contains 50·43% of pentosan and 21·85% of galactan, and yields *l*-arabinose and *d*-galactose by hydrolysis.

The gum from *Melia Azadirachta*, grown in the Deccan, Ceylon, and the Malay Archipelago, contains moisture 15·41%, ash 2·99% (Ca 0·76%; Mg 0·294%), and 0·27% of matter insoluble in water. The aqueous solution has α_D −57·16° ($p=7·958$ and $D=1·0332$). It contains 11·11% of galactan, 26·27% of pentosan, and yields *l*-arabinose and *d*-galactose by hydrolysis.

The preceding gums respond to Lassaigne's test for nitrogen when potassium is used instead of sodium (compare Stevens, Abstr., 1905, i, 574; Bach, Abstr., 1908, i, 238). C. S.

Conversion of Cellulose into Sugar. HERMANN OST and L. WILKENING (*Chem. Zeit.*, 1910, **34**, 461—462).—The hydrolysis of cellulose by heating in an autoclave with dilute sulphuric acid is unsatisfactory, since at the high temperature necessary, dextrose is in part converted into reversion products and in part into acids and humus substances. Flechsig's method, the conversion of cellulose by cold concentrated sulphuric acid into dextrins and the hydrolysis of these by boiling with dilute acids, has been adversely criticised by Schwalbe and Schulz (this vol., i, 301), but it is now shown that treatment for three hours with 72% sulphuric acid and then for one hour with 2—3% of acid gives almost theoretical yields of dextrose, and after neutralisation and fermentation, over 80% of the theoretical quantity of alcohol. The purity of the dextrose was controlled by the phenylosazone test and by the optical rotatory power. E. F. A.

New Cellulose Derivatives of Low Nitrogen Contents. JASPER E. CRANE and CLARENCE M. JOYCE (*J. Soc. Chem. Ind.*, 1910, **29**, 540—542. Compare Hake and Bell, Abstr., 1909, i, 457).—A *product*, $C_{12}H_{21}O_{13}N$, probably $C_{12}H_{19}O_9 \cdot NO_3, H_2O$, is obtained by the following process. Cellulose, in the form of purified cotton yarn, high grade cotton, tissue paper, or Swedish filter paper, is immersed for a few seconds in a mixture containing 65·5% sulphuric acid, 9% of nitric acid, and 25·5% of water. After removal, the product is drained for twelve minutes at 10°, when it becomes quite gelatinous; it is then plunged into cold water, producing a white, curdy precipitate, which is purified by solution in dilute sodium hydroxide, precipitation by means of hydrochloric acid, and extraction with alcohol and ether or acetone.

It forms a hard, white powder, dissolves in concentrated acids or strong alkalis, in certain phenols, and in Schweitzer's reagent or in zinc chloride solution. The solution in sodium hydroxide, when kept for some time, yields products soluble in water. The nitrocellulose reacts vigorously with acetic anhydride and a little water, yielding an *acetyl* derivative, $C_{22}H_{31}O_{18}N$, which dissolves readily in acetone.

The compound obtained is the lowest cellulose nitrate yet prepared, and in properties resembles cellulose hydrates rather than the nitrates.

A brief summary of the products formed by the action of concentrated sulphuric acid, concentrated nitric acid, and of dilute acids is given. The conclusion is drawn that the important factor in the action of acids is the percentage of water in the acid. With 20—40% of water, hydrates are formed, but with 50—60% of water, hydrolysis occurs and hydrocelluloses are formed. With the mixed acids each acid endeavours to carry out its characteristic function, and at the same time the water present tends to hydration or hydrolysis, according to the amount present. The formation of the nitrate described above is due to the sulphuric acid dissolving the cellulose, forming sulphuric esters, which are decomposed by the water to cellulose hydrates, and these in their turn are converted into nitrates.

J. J. S.

Platinichlorides and Periodides of Di- and Tri-methylamine and their Employment in the Separation of the Bases. JEAN BERTHEAUME (*Compt. rend.*, 1910, **150**, 1063—1065).—Details are given of the solubility in alcohol of the platinichlorides of di- and tri-methylamine at different temperatures. The small difference in solubility of these salts renders useless the methods proposed by Bresler (*Ann. Chim. anal.*, 1901, [vi], 28) and Eisenberg (Abstr., 1881, 246) for separating the bases. For the same reason the method of Weiss (*Annalen*, 1892, **267**, 258), based on differences in the solubility of the periodides, is said to be unsatisfactory.

Dimethylamine periodide, $NHMe_2,HI,I_3$, is stable, and crystallises in hexagonal tablets, m. p. 83—85°; like the corresponding trimethyl-compound, its solubility is considerably lowered by the presence of magnesium sulphate or of alkali chlorides. W. O. W.

Compounds of Hexamethylenetetramine with Mercuric Salts. ED. SCHMIZ (*Ber. deut. Pharm. Ges.*, 1910, **20**, 201—202).—In extension of the work of Grishkewitsch-Trochimowsky (this vol., i, 108) and Riedel (D.R.-P. 217897), the author describes additive products of this amine with mercuric chloride, iodide, and sulphate, formed by mixing dilute solutions of the amine and the salt in each case.

The *mercuric chloride* compound, $C_6H_{12}N_4,2HgCl_2$, crystallises in colourless needles, is sparingly soluble in water, more so on addition of ammonium chloride, decomposes when heated in water at 80°, and evolves formaldehyde when warmed with dilute sulphuric acid.

The *mercuric iodide* compound, $C_6H_{12}N_4,2HgI_2$, forms small yellowish-white needles, and the *mercuric sulphate* compound, of analogous composition, occurs in colourless, silky needles. T. A. H.

Compounds of Amino-acids and Ammonia. V. PETER BERGELL and HANNS VON WULFING (*Zeitsch. physiol. Chem.*, 1910, **65**, 489—496. Compare this vol., i, 304).—*Chloroacetyl-leucinamide*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained from chloroacetyl chloride, leucinamide hydrobromide, and alkali, crystallises from dilute alcohol in nacreous plates, m. p. 157° (corr.), and when shaken for six hours with 25% aqueous ammonia and the mixture kept for twelve hours at 40°, yields *glycyl*-d-l-*leucinamide*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO\cdot NH_2)\cdot CH_2\cdot CHMe_2$, as the *hydrochloride*, which crystallises in minute plates, m. p. 211—212° (corr.)

Bromopropionyl-lencinamide,

$$CHMeBr\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained by the action of bromopropionyl bromide on leucinamide hydrobromide and alkali, crystallises in slender needles, m. p. 150—151° (corr.), and with ammonia yields *alanyl leucinamide hydrobromide*,

$$HBr,NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

which melts at 140° when anhydrous.

Chloroacetylglycyl-leucinamide,

$$CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\cdot NH_2,$$

obtained from glycyl-leucinamide hydrochloride and chloroacetyl chloride, crystallises in minute needles, m. p. 190—191° (corr.).

In many of these preparations it is not necessary to isolate the amino-compound in the pure state; for example, for the preparation of chloroacetyl-leucinamide, it is merely necessary to heat bromo*iso*-hexoamide with alcoholic ammonia at 105—110°, to evaporate under reduced pressure, extract the residue with a little water, and to treat the clear aqueous solution with chloroacetyl chloride and alkali.

The chloroacetyl derivatives are of use in detecting amides of amino-acids and peptides. J. J. S.

Behaviour of Racemic Aspartic Acid on Putrefaction. CARL NEUBERG (*Archiv. Fisiol.*, 1909, 7, 87—90).—By ordinary putrefactive bacteria, inactive aspartic acid was not decomposed into optically active components. W. D. H.

The *cyclo*Octane Series. IV. RICHARD WILLSTÄTTER and ERNST WASER (*Ber.*, 1910, **43**, 1176—1183).—The authors have undertaken the preparation of *cyclo*octene, which is an important member of this group (compare Harries, Abstr., 1907, i, 35), by the method of reduction with platinum-black previously employed (Abstr., 1908, i, 383, 636), and they have used the same means to obtain tropane and α-dimethylaminopentane.

Δ^4-*des*-Dimethylgranatanine, $C_8H_{13}NMe_2$ (compare Willstätter and Veraguth, Abstr., 1905, i, 515, 543), has b. p. 80°/9 mm., 95°/19 mm., or 210—210·5°/760 mm., and d_4^0 0·910 (rather lower than formerly given). On shaking this substance for at least a day with platinum-black in an atmosphere of hydrogen, *dimethylamino*cyclo*octane* was obtained as a mobile oil, b. p. 86—86·5°/11 mm., or 216—217°/760 mm. It has d_4^0 0·900, d_4^{20} 0·883, n_D^{20} 1·4790. Its *platinichloride* has m. p. 183—184°, and the *methiodide*, 270—271° (decomp.). On distilling the *quaternary ammonium hydroxide* (from the above methiodide), cyclo*octene* is produced, b. p. 143·5°/730 mm. (corr. 145°). It has d_4^0 0·871, d_4^{20} 0·855, n_D^{20} 1·4739. The substance polymerises easily.

*Bromo*cyclo*octane*, $C_8H_{15}Br$, is formed quantitatively from *cyclo*-octene and hydrobromic acid in glacial acetic acid. It is an oil, b. p. 90·5—91·5°/10 mm. It has d_4^0 1·309, d_4^{20} 1·290, n_D^{20} 1·5112, and yields with magnesium and carbon dioxide a cyclo*octanecarboxylic acid*, which is being investigated. cyclo*Octane*, C_8H_{16}, is obtained by reducing *cyclo*octene, as above described, in purer form than by the method formerly employed (Willstätter and Veraguth, Abstr., 1907, i, 303), and has b. p. 147·3—148·3°/709 mm. (corr. 149·6—150·6°), m. p. 14·2—14·4°, d_4^{20} 0·839, n_D^{20} 1·4586.

By reducing tropidine in the same way, tropane is readily prepared. It has b. p. 163—165° (corr.).

α-*Dimethylaminopentane* (from dimethylpiperidine) has b. p. 122—123° (corr.), d_4^0 0·755, d_4^{20} 0·743, n_D^{20} 1·4083. The *platinichloride* has m. p. 127—128°, and the *methiodide*, m. p. 222—223°.

R. V. S.

Δ^3-*cyclo*Hexene Derivatives. W. SOBECKI (*Ber.*, 1910, **43**, 1038—1041).—When potassium phthalimide is heated for six to

eight hours at 180—190° with 1 : 4-dibromo*cyclo*hexane, substituted derivatives of *cyclo*hexane are not obtained, but hydrogen bromide is eliminated and phthalimide and Δ^3-bromo*cyclo*hexene are formed. When the dibromo-derivative is heated with quinoline, the chief product is *cyclo*hexadiene.

Δ^3-*Bromo*cyclo*hexene*, C_6H_9Br, is a colourless, highly refractive liquid, with b. p. 54—54·5°/15 mm., and D_4^{15} 1·3772. It distils at 160—163° under atmospheric pressure, but is partly decomposed. It has an odour of allyl bromide, and turns brown when kept for several weeks. With alcohol and concentrated sulphuric acid it gives an intense red coloration. The *dibromide*, $C_6H_9Br_3$, is an oil. The bromo*cyclo*hexene forms a Grignard compound, and this reacts with carbon dioxide, yielding Δ^3-*cyclo*hexenoic acid (W. H. Perkin, Trans., 1904, **85**, 431).

A small yield of Δ^3-cyclo*hexenaldehyde*, $C_7H_{10}O$, can be obtained by the action of ethyl orthoformate on the Grignard compound from Δ^3-bromo*cyclo*hexene in the presence of dry toluene, and subsequent hydrolysis of the acetal. It has b. p. 58°/17 mm. and D_4^{15} 0·9524; it is characterised by an extremely disagreeable odour, readily polymerises, and yields a *semicarbazone*, $C_8H_{13}ON_3$, m. p. 153·5—154·5°.

J. J. S.

Some Hydrocarbons of the Diphenyl Series. Erling Schreiner (*J. pr. Chem.*, 1910, [ii], **81**, 422—424).—The following hydrocarbons have been prepared by heating iodo-compounds with "Naturkupfer" (copper bronze) in a glass flask : 4 : 4′-*Diethyldiphenyl*, $C_6H_4Et{\cdot}C_6H_4Et$, m. p. 80°, from *p*-iodoethylbenzene ; 4 : 4′-*di*iso*propyldiphenyl*, m. p. 49°, from *p*-iodo*iso*propylbenzene ; 4 : 4′-*di*tert.-*butyldiphenyl*, m. p. 122°, from *p*-iodo*tert.*-butylbenzene. All three are colourless, crystalline substances. C. S.

Hydrocarbons from ω-Bromostyrene and Preparation of γ-Phenylbutyric Acid. Hans Rupe and H. Proske (*Ber.*, 1910, **43**, 1231—1234).—Rupe and Bürgin (this vol., i, 161) have shown that by the action of magnesium on cinnamyl chloride, a branched-chain hydrocarbon, *a*,δ-diphenyl-Δ^a-hexene, is the main product.

By the action of magnesium on ω-bromostyrene, the main product is styrene, but a certain amount of the normal magnesium halogen compound interacts with a second molecule of bromostyrene, forming *a*δ-diphenyl-$\Delta^{a\gamma}$-butadiene, CHPh:CH·CH:CHPh, crystallising in nacreous plates, m. p. 147—148°.

Phenylbutyric acid is readily obtained by the interaction of γ-bromo-*a*-phenylpropane and magnesium in ether, saturation with carbon dioxide, and subsequent hydrolysis; it crystallises in colourless, fatty, lustrous plates, m. p. 52°. E. F. A.

Triphenylmethyl, Triphenylacetaldehyde, and Triphenylacetic Anhydride. Julius Schmidlin (*Ber.*, 1910, **43**, 1137—1144).—Triphenylacetyl chloride (Schmidlin and Hodgson, Abstr., 1908, i, 170) when treated with magnesium phenyl iodide does not yield

β-benzopinacolin, as would be expected, but carbon monoxide is split off and triphenylmethyl is formed. The triphenylmethyl is isolated from ethereal solution in crystals containing ether of crystallisation. The substance has the formula $2CPh_3,Et_2O$, and m. p. 85—90° (with liberation of ether). Only in one experiment was a trace of β-benzopinacolin produced. When the reaction is carried out at the b. p. of ether, triphenylcarbinol and triphenylmethane are obtained. The removal of carbon monoxide from triphenylacetyl chloride is also effected by molecular silver; a small quantity of triphenylacetic anhydride may be formed as a by-product.

The Grignard reaction with triphenylacetyl chloride proceeds normally when, instead of the iodide, magnesium phenyl bromide is employed. β-Benzopinacolin is obtained, and no trace of carbon monoxide is evolved. The author finds other instances of this difference between iodide and bromide (compare following abstract). *p*-Benzoyltriphenylmethane reacts with magnesium phenyl bromide, but not with the iodide. Whilst magnesium phenyl bromide and ω-chlorotriphenylmethane yield tetraphenylmethane (Gomberg, Abstr., 1906, i, 414; Freund, Abstr., 1906, i, 574), the action of magnesium phenyl iodide on ω-chlorotriphenylmethane yields triphenylmethyl (which may be prepared in this way) according to the equation: $CPh_3Cl + 2PhMgI = 2CPh_3 + Ph_2 + 2MgICl$. The production of diphenyl was observed.

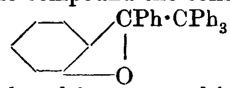
The action of magnesium ethyl iodide on triphenylacetyl chloride yields *triphenylmethyl ethyl ketone*, m. p. 103—104° (corr.).

Triphenylacetic anhydride, prepared from *silver triphenylacetate* and triphenylacetyl chloride, has m. p. 163° (corr.), with effervescence due to splitting off of carbon monoxide. It is hydrolysed with difficulty.

Magnesium triphenylmethyl chloride reacts with ethyl formate, yielding *triphenylacetaldehyde* in small laminæ (from ether), m. p. 223·5° (corr.), with development of a red coloration and evolution of carbon monoxide. The mother liquors contain a *substance* which, with concentrated sulphuric acid, gives an intense bluish-green coloration, becoming red. The aldehyde, like diphenylacetaldehyde (Breuer and Zincke, Abstr., 1880, 118), cannot be oxidised to the corresponding acid. R. V. S.

Pentaphenylethanol. JULIUS SCHMIDLIN and JULIUS WOHL (*Ber.*, 1910, **43**, 1145—1152).—The preparation of this compound has been effected from β-benzopinacolin and magnesium phenyl iodide, although the use of the bromide is impossible for this purpose (compare Gomberg, Abstr., 1906, i, 414; also Abstr., 1907, i, 27, and preceding abstract). For the reaction a large excess (7—8 molecules) of the iodide must be taken, and solution only takes place after boiling has been continued for twenty hours. The raw product is purified by means of light petroleum, and recrystallised from ether and from benzene. Pure *pentaphenylethanol* forms colourless prisms, m. p. 179° (corr.), and remains unaltered when kept for some time at the m. p. Impure specimens gradually decompose when kept for a long time at the ordinary temperature. On distillation in a vacuum the

substance yields triphenylmethane. The hydroxyl group does not condense with amines or phenols, and cannot be replaced. On heating the compound with very concentrated hydrobromic acid, halogen is introduced, but without replacing the hydroxyl group. Hydrochloric acid, acetyl chloride, and phosphorus pentachloride all yield a stable substance, *dehydropentaphenylethanol*, containing two hydrogen atoms less in the molecule. The same substance is found in the mother liquors in the preparation of pentaphenylethanol. It forms hard, lustrous crystals, m. p. 188° (corr.), and gives a green coloration with sulphuric acid. On oxidation β-benzopinacolin is formed, and hence the authors ascribe to the compound the constitution:



Dehydropentaphenylethanol is converted by sulphuric acid into an isomeride, iso*dehydropentaphenylethanol*, which crystallises with $1\frac{1}{2}$ molecules of benzene of crystallisation in short, thick prisms, m. p. 238° (corr.), the benzene being evolved previously at a much lower temperature. This isomeride is also formed when pentaphenylethanol is shaken in benzene solution with sulphuric acid.

When triphenylmethyl peroxide is distilled in a vacuum, the distillate contains phenol, whilst the residue consists chiefly of tetraphenylethylene; triphenylmethane was not found to be present.

Further investigation of the substance formerly (*loc. cit.*) described as being possibly hexaphenylethane containing admixed magnesium has not justified that supposition. R. V. S.

$\alpha\beta$-Dichlorotetraphenylethane, the Chlorine Derivative of α-Benzopinacolin. JULIUS SCHMIDLIN and ROBERT VON ESCHER (*Ber.*, 1910, **43**, 1153—1161).—When diphenyldichloromethane (from benzophenone) is shaken for a long time (thirty-six hours) with molecular silver (1 molecule), *$\alpha\beta$-dichloro-s-tetraphenylethane* is produced. The liquid must be kept homogeneous by shaking until the reaction is complete, otherwise only tetraphenylethylene and unchanged diphenyldichloromethane are obtained. $\alpha\beta$-Dichloro-*s*-tetraphenylethane has m. p. 186° (corr.), with evolution of hydrogen chloride. It forms crystals containing one molecule of benzene of crystallisation. It is soluble in concentrated sulphuric acid and in cold acetic acid, but when boiled with the latter, hydrogen chloride is evolved, with formation of a monochloride. Boiling water also causes chlorine to split off, yielding α-benzopinacolin, but no reaction takes place with moist silver oxide or with silver acetate. The action of silver on $\alpha\beta$-dichloro-*s*-tetraphenylethane leads to the production of tetraphenylethylene, which is also formed when the substance is distilled, and when it is acted on by aliphatic or aromatic Grignard solutions or by phenylhydrazine. With benzene and aluminium chloride, an unusual reaction occurs, 9 : 10-diphenylphenanthrene (compare Werner and Grob, Abstr., 1904, i, 864) being produced. The monochloro-compound also yields 9 : 10-diphenylphenanthrene under these conditions.

The constitution of the *monochloro*-compound, $C_{26}H_{19}Cl$, obtained

from tetraphenyldichloroethane as above-mentioned, has not been settled. It has m. p. 187° (corr.), without evolution of gas, and on boiling with water no chlorine is evolved. The compound could not be obtained free from *a*-benzopinacolin. *aβ*-Dichlorotetraphenylethane when heated with phenol also gives this monochloro-compound, whilst with aniline a small amount of a hydrocarbon was obtained in glittering, green needles, m. p. 145°. R. V. S.

Perchloric Acid as a Reagent in Organic Chemistry. KARL A. HOFMANN, AUGUST METZLER, and KURT HÖBOLD (*Ber.*, 1910, **43**, 1080—1086).—Perchlorates possess many advantages over picrates for the separation of carbinols, ketones, and amines in a state of purity. They are obtained by treating solutions in ether, benzene, tetrachloroethane, or carbon tetrachloride with 70% perchloric acid, or even using the concentrated acid alone or mixed with acetic acid as solvent. As a class they crystallise well and are not dangerous. To eliminate the perchloric acid, it suffices to wash feebly basic substances with water, or strongly basic substances are shaken with potassium carbonate or calcium oxide in a suitable solvent. They are analysed by fusing with sodium carbonate in a platinum crucible and estimating the chlorine.

Coerulignone diperchlorate forms green, glistening, dark blue crystals. *Gallein perchlorate* crystallises in lancet-shaped plates of a metallic green lustre, but red in transmitted light; it is doubly refractive, and yields a red ethereal solution.

Isatin perchlorate forms yellow or almost colourless, four-cornered, obliquely-cut prisms. Indigotin yields a *perchlorate* in the form of a bluish-black powder.

a-Methylindole perchlorate separates in flat, colourless, lustrous prisms, decomp. 170°.

Acridine perchlorate crystallises from glacial acetic acid in thick, four-cornered, yellow prisms, or from carbon tetrachloride in greenish-yellow, hexagonal plates.

Phenazine diperchlorate is a deep red, crystalline powder with a bluish reflex; it becomes yellow when exposed to the atmosphere. The colour of this diperchlorate is in marked contrast to that of the simple acid salts of phenazine.

Azobenzene perchlorate is a yellow powder, consisting of doubly refractive, wine-yellow plates.

Triphenylamine monoperchlorate, $C_{18}H_{15}N,ClO_4H$, forms colourless crystals exploding at 180°. The formation of this salt shows that triphenylamine still has basic properties. *Triphenylamine hemiperchlorate*, $2(C_{18}H_{15}N),ClO_4H$, forms cubical or octahedral crystals of greenish lustre, decomp. 220°. The green coloration is regarded as an impurity. p-*Tritolylamine monoperchlorate* separates in almost colourless, granular crystals, which explode at about 180°; a *hemiperchlorate* forms bright green, lustrous prisms. When a large excess of perchloric acid is used, a *diperchlorate*, $C_{20}H_{21}N,2ClO_4H$, is obtained, crystallising in steel-blue or bluish green, flat prisms, but this coloration is attributed to associated impurity. Tritolylamine, therefore, has basic properties, and forms normal colourless salts.

Diphenylamine perchlorate separates in clear, colourless, cubical crystals; when exposed to light, it only very slowly becomes faintly blue.

Perchloric acid (70%) has hardly any oxidising action at the ordinary temperature, and does not, for example, affect quinol or trichloroquinone. Chrysene by crystallisation from perchloric acid is obtained in colourless, silver, glistening, irridescent platelets, m. p. 250°.

Diphenylfulvene, dissolved in glacial acetic acid and treated with perchloric acid, forms a bright green powder, possibly the perchlorate, but the original substance is not re-formed on hydrolysis. E. F. A.

Derivatives of Amino-acids. EMIL ABDERHALDEN and PAUL BLUMBERG (*Zeitsch. physiol. Chem.*, 1910, **65**, 318—322).—The authors have investigated the compounds formed by the action of chlorodinitrobenzene on amino-acids, in the hope of discovering substances which would facilitate the isolation of the latter from urine. The undermentioned compounds, however, crystallise well only when prepared from the pure amino-acids. The reaction is effected by heating together for two hours an aqueous solution of 1 molecule of amino-acid and 2 molecules of sodium hydrogen carbonate, and an alcoholic solution containing 1 molecule of chlorodinitrobenzene. After evaporation, the residue is dissolved in water, and precipitated with hydrochloric acid, the product being recrystallised from acetic acid and water. 2 : 4-*Dinitrophenylglycine* forms golden crystals, m. p. 205°, the yield being 70%. 2 : 4-*Dinitrophenylglycine ethyl* ester crystallises in greenish-yellow needles, m. p. 144°; yield 85%. 2 : 4-*Dinitrophenyl*-dl-*alanine* forms small, golden laminæ, m. p. 178°; yield 60%. 2 : 4-*Dinitrophenyl*-dl-*valine* also crystallises in golden laminæ, m. p. 185° (previously sintering); the yield is 85%. 2 : 4-*Dinitrophenyl*-dl-*leucine* forms yellow crystals with a greenish lustre, m. p. 203° (with production of a red coloration). 2 : 4-*Dinitrophenylasparagine* has m. p. 191—192°; yield 60%.

With histidine two derivatives are obtained. *Mono*-2 : 4-*dinitrophenylhistidine* crystallises in long, red needles. *Di*-2 : 4-*dinitrophenylhistidine* forms greenish-yellow crystals, which decompose at 250°. 2 : 4-*Dinitrophenyl*-dl-*leucine* crystallises in greenish-yellow laminæ, m. p. 169° (previously sintering); yield 60%. R. V. S.

Preparation of 5-Halogen-6-chloro-2-acylaminotoluenes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 217896).—The halogenation in a convenient solvent of 6-chloro-2-acyltoluidines with either chlorine or bromine yields compounds which contain the second halogen atom in the para-position to the acylamino-group. The preparation of 5 : 6-*dichloroaceto*-o-*toluidide*, needles, m. p. 144—145°, and of 6-*chloro*-5-*bromoaceto*-o-*toluidide*, m. p. 154—155°, is described in the patent.
F. M. G. M.

[Preparation of 3-Chloro-*o*-toluidine-5-sulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 218370).—3-*Chloro*-o-*toluidine*-5-*sulphonic acid* is prepared by treating 2-acylamino-5-toluenesulphonic acids in aqueous solution with chlorine and subsequent

hydrolysis of the acyl group; it forms needles which are readily soluble in hot water; by heating with 75% sulphuric acid at 150—160°, the sulphonic group is removed, yielding 3-chloro-*o*-toluidine.

F. M. G. M.

Preparation of Optically Inactive *o*-Dihydroxyphenylalkylamines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 220355).—The synthetic *o*-dihydroxyphenylalkylamines are optically inactive, and their resolution into the required components is important, as, contrary to the opinion generally held, the dextro-compounds possess valuable therapeutic properties.

It is found that both the dextro- and the lævo-compound can be racemised by treatment with sulphuric or hydrochloric acid; the inactive mixture is then resolved into the active components, and the isomeride which is not required again racemised and subsequently resolved, the process being repeated indefinitely. Examples are given of the racemisation of *l*-*o*-dihydroxyphenylethanolmethylamine (*l*-adrenaline), $\alpha_D' -50°$, of *d*-adrenaline, and of natural *l*-adrenaline, in which the base is treated with 1·5 mols. of hydrochloric acid in water and the temperature maintained at 80—90° during several hours.

F. M. G. M.

Influence of Constitution on the Velocity of Decomposition of Quaternary Ammonium Salts. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1910, 43, 1303—1312. Compare Abstr., 1906, i, 14, 161, 419; also Halban, Abstr., 1907, ii, 246; 1908, i, 627).—A comparison of the rates of racemisation of the isomeric *l*-phenylbenzylmethyl-*n*-butylammonium iodide and *l*-phenylbenzylmethyl*iso*butylammonium iodide in chloroform solution at 25° shows that the *iso*butyl derivative is racemised about four times as quickly as its isomeride.

The rates of decomposition of a number of quaternary ammonium salts into tertiary amine and alkyl halide have been determined in dilute (1—2%) chloroform solution at 35° and 45°. The method adopted was, at the end of given periods of time, to extract the chloroform solution (5 or 10 c.c.) twice with 125 c.c. of water, to mix the two aqueous extracts, and titrate with silver nitrate according to Volhard's method. The water extracts the ionised ammonium salts, whereas the products of decomposition are retained by the chloroform. The addition of alcohol, as recommended by von Halban, is not advisable, as it lowers the rate of dissociation. The following salts are quite stable in dilute chloroform solution, namely: tetraethyl-, triethylallyl-, benzyltriethyl-, and methyldiethyl-phenylammonium iodide. For other salts the following constants were obtained:

	K. 35°	*K.* 45°
Phenylbenzyldiethylammonium bromide	$1·7 \times 10^{-3}$	$6·5 \times 10^{-3}$
Phenylbenzyldimethylammonium bromide		$1·3 \times 10^{-3}$
Phenylbenzyldiethylammonium iodide	$9·9 \times 10^{-3}$	$3·5 \times 10^{-2}$
Phenyldibenzylmethylammonium iodide	$5·3 \times 10^{-3}$	
Phenyldiethylallylammonium iodide	$4·1 \times 10^{-4}$	$1·6 \times 10^{-3}$

It is thus clear that only those salts undergo measurable decomposition which contain both a phenyl group and also an unsaturated group, such as benzyl or allyl.

Of the phenylbenzyldialkylammonium salts, the dimethyl is the most stable, the replacement of one methyl group by a propyl, *n*-butyl, or an allyl group doubles the value of *K*, and the replacement of two methyl by two ethyl groups increases *K* in the ratio 1 : 5.

The decomposition of phenylbenzyldiethylammonium bromide in chloroform solution has been studied in detail, and the conclusion is drawn that the products of dissociation are diethylaniline and benzyl bromide.

It is pointed out that those salts which are most readily dissociated in chloroform solution are the salts which are most readily resolved into their optically active components.

Methylallyltetrahydroquinolinium iodide (Abstr., 1907, i, 1073), which racemises extremely readily in methyl alcoholic solution, appears to undergo but slight dissociation in the same solvent. J. J. S.

Replacement of Halogen by the Nitro-group. I. L. CHAS. RAIFORD and FREDERICK W. HEYL (*Amer. Chem. J.*, 1910, **43**, 393—398).—It has been shown by Armstrong and Harrow (Abstr., 1876, i, 477) that nitric acid reacts with 2 : 4 : 6-tribromophenol with formation of 2 : 6-dibromo-4-nitrophenol. Claus and Hirsch (Abstr., 1889, 389) found that 2 : 4 : 6-tribromo-*m*-cresol is similarly converted into 2 : 6-dibromo-4-nitro-*m*-cresol, whilst by the action of nitrous acid on the same tribromo-compound, Zincke (Abstr., 1900, i, 545) also obtained a dibromo-4-nitro-*m*-cresol.

On repeating Zincke's work at 12—15°, a mixture of two nitro-derivatives has been obtained, in which the nitro-groups are in the ortho- and para-positions respectively to the hydroxyl group.

When sodium nitrite is added gradually to a solution of 2 : 4 : 6-tribromophenol in glacial acetic acid at 12—15°, a mixture of 4 : 6-dibromo-2-nitrophenol, m. p. 117°, and 2 : 6-dibromo-4-nitrophenol, m. p. 141°, is obtained. 2 : 4 : 6-Trichlorophenol does not react with nitrous acid under these conditions. E. G.

Preparation of Glycerol Mono-*o*- and -*p*-chlorophenyl Ethers. LES ETABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 219325).—The chlorophenyl glycerol ethers,

$$C_6H_4\cdot Cl\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

prepared from glycerol monochlorohydrin and the alkali salts of *o*- or *p*-chlorophenol, have valuable therapeutic properties, being tasteless and odourless, whereas the corresponding glycerol phenyl ethers have a bitter taste in aqueous solution.

Glycerol p-*chlorophenyl ether* crystallises from a mixture of ether and petroleum in colourless needles, m. p. 80°, b. p. 214—215°/19 mm.

Glycerol o-*chlorophenyl ether* has m. p. 65°, and b. p. 250°/19 mm.

F. M. G. M.

[Preparation of Amino-derivatives of Aromatic Ethers.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 220722. Compare this vol., i, 312).—A description of the preparation of dyes

from diazotised aromatic amino-ethers coupled with pyrazolone-sulphonic acids, and naphthylpyrazolonesulphonic acids.

The following new ethers are described:

2-*Aminophenyl* o-*tolyl ether*, a yellow oil, b. p. 196°/23 mm.; it does not solidify at −13°.

2-*Aminophenyl* m-*tolyl ether*, a colourless, slowly crystallising oil, b. p. 204°/34 mm., m. p. 30°.

2-*Aminophenyl* p-*tolyl ether*, yellow oil, b. p. 193°/20 mm., does not solidify at −13°.

4-*Aminophenyl* o-*tolyl ether*, colourless crystals, m. p. 62°.

4-*Aminophenyl* m-*tolyl ether*, m. p. 79°.

4-*Aminophenyl* p-*tolyl ether*, colourless needles, m. p. 121·5°.

2-*Amino-4-sulphophenyl* o-*tolyl ether*, prepared from *o*-chloronitrobenzenesulphonic acid and *o*-cresol; the free acid is insoluble in water and alcohol; the *barium* salt forms colourless leaflets.

F. M. G. M.

Action of Sulphur and Selenium on Magnesium *cyclo*Hexyl Chloride. ALPHONSE MAILHE and M. MURAT (*Bull. Soc. chim.*, 1910, [iv], 7, 288—291).—The action of precipitated sulphur on magnesium *cyclo*hexyl chloride is analogous with that on organo-magnesium haloids in general (Wuyts, Abstr., 1909, i, 380).

cyclo*Hexyl mercaptan*, D^0 0·9905, D^{20} 0·9782, n_D 1·481, b. p. 150—152°/152 mm., is the chief product; it is a colourless liquid of unpleasant alliaceous odour, and furnishes with solutions of metallic salts, *mercaptides* of the general formula $C_6H_{11}SM'$, which are usually different in colour from the corresponding metallic sulphides. Phosphoric acid or anhydride decomposes the mercaptan, forming *cyclo*hexene. On heating in a reflux apparatus with acetic acid, the mercaptan is slowly decomposed, with the formation of hydrogen sulphide and *cyclo*hexyl acetate. On oxidation by dilute nitric acid or chromic acid, or by the action of iodine on the sodium derivative of the mercaptan, cyclo*hexyl disulphide*, $(C_6H_{11})_2S_2$, b. p. 288°, is formed.

Selenium acts on magnesium *cyclo*hexyl chloride in an analogous manner, forming the corresponding *selenol*, $C_6H_{11}{\cdot}SeH$, D^0 1·1223, b. p. 170—172°, which closely resembles the thiol in properties, and furnishes with metallic salts, metallic *derivatives* of the general formula $C_6H_{11}SeM'$, which are generally of the same colour, but darker than the corresponding mercaptides. No diselenide could be obtained by oxidation of the selenol.

The fact that *cyclo*hexanol has a boiling point intermediate between those of the thiol and the selenol indicates that its molecule is polymerised, since normally it should boil below the thiol.

T. A. H.

Phenolic Ethers Containing the ψ-Allyl Side-chain, $CMe{:}CH_2$. *o*-Hydroxytoluic Series. IV. AUGUSTE BÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1910, [iv], 7, 330—332).—The anomalous physical properties of certain of the *o*-hydroxytoluic derivatives described in a previous paper (Abstr., 1908, i, 630) have led the

authors to repeat their work, and the following new constants are given for the compounds.

Methyl *o*-hydroxytoluate (m. p. 0°) gives with magnesium methyl iodide, 3-ψ-allyl-*o*-cresol, D^0 0·9952, b. p. 100—102°/14 mm. or 211—213°/760 mm., which colours ferric chloride solution orange-red. Its methyl ether has D^0 0·972 and b. p. 208—210°, and is readily reduced by sodium in alcohol, giving *o*-thymyl methyl ether, D^0 0·9518, b. p. 210—212°, and this on demethylation gives *o*-thymol (*iso*thymol), D^0 1·9924 (see succeeding abstract), b. p. 225—226°, which colours ferric chloride orange-yellow, and with sodium and chloroacetic acid furnishes o-*thymyloxyacetic acid*, m. p. 84°. The different physical properties previously ascribed were due to the use of *o*-hydroxytoluic acid containing the *m*-isomeride. T. A. H.

Two New Isomerides of Thymol. 2-Hydroxy-1-methyl-3-*iso*propylbenzene (*o*-Thymol) and 4-Hydroxy-1-methyl-3-*iso*propylbenzene (*p*-Thymol). G. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], 7, 332—342).—The author has applied Béhal and Tiffeneau's method of synthesis (Abstr., 1908, i, 630) to *o*- and *p*-hydroxytoluic acids, and obtained in this way *o*- and *p*-thymols, isomeric with ordinary *m*-thymol already synthesised in like manner from *m*-hydroxytoluic acid (*loc. cit.*).

Methyl o-*methoxytoluate*, $OMe{\cdot}C_6H_3Me{\cdot}CO_2Me(2:1:3)$, D^0 1·1258, $D^{17\cdot4}$ 1·1102, $n_D^{17\cdot4}$ 1·51664, b. p. 249·5—250·5°/763 mm. (corr.) or 129—131°/14 mm. (corr.), is a limpid, almost colourless liquid, which with magnesium methyl iodide furnishes the corresponding *tertiary alcohol*, $OMe{\cdot}C_6H_3Me{\cdot}CMe_2{\cdot}OH(2:1:3)$, D^0 1·0542, $D^{14\cdot8}$ 1·0420, $n_D^{14\cdot8}$ 1·52147, b. p. 131—132°/14 mm. (corr.) or 239—243°/760 mm. (decomp.), a pleasant smelling, thick liquid, that on dehydration by hot acetic anhydride gives 2-*methoxy*-1-*methyl*-3-ψ-*allylbenzene*, D^0 0·9713, D^{15} 0·9599, n_D^{15} 1·52049, b. p. 96—99°/14 mm. (corr.) or 209—210°/762 mm. (corr.), a colourless, mobile, pungent-smelling liquid. On reduction this furnishes 2-methoxy-1-methyl-3-*iso*propylbenzene (*o*-thymyl methyl ether), D^0 0·9515, $D^{14\cdot6}$ 0·9397, $n_D^{14\cdot6}$ 1·50063, b. p. 210—211°/760 mm. (corr.), a colourless, pleasant smelling liquid (compare Béhal and Tiffeneau, preceding abstract). On demethylation it yields 2-hydroxy-1-methyl-3-*iso*propylbenzene (*o*-thymol), D^0 0·9986, $D_D^{15\cdot2}$ 0·9865, $n_D^{15\cdot2}$ 1·52385, b. p. 225—226°/760 mm. (corr.), a colourless liquid, which becomes green when kept, and has an odour recalling that of *o*-cresol (*loc. cit.*).

3-*Methoxymethyl*-p-*toluic acid*, $OMe{\cdot}C_6H_3Me{\cdot}CO_2Me(3:1:4)$, D^0 1·1430, $D^{17\cdot2}$ 1·1287, $n_D^{17\cdot2}$ 1·53016, b. p. 143—146°/14 mm. (corr.) or 263—265°/760 mm. (corr.), is a colourless, almost inodorous liquid. With magnesium methyl iodide it yields the *tertiary alcohol*, $OMe{\cdot}C_6H_3Me{\cdot}CMe_2{\cdot}OH(3:1:4)$, D^0 1·0440, D^{15} 1·0321, n_D^{15} 1·52094, b. p. 134—136°/14 mm. (corr.), which is a viscid, colourless, pleasant-smelling liquid. On dehydration it yields 3-*methoxy*-1-*methyl*-4-ψ-*allylbenzene*, D^0 0·9806, $D^{15\cdot8}$ 0·9676, $n_D^{15\cdot8}$ 1·53148, b. p. 105—107°/13 mm. (corr.) or 218—220°/760 mm. (corr.), and this on reduction yields the corresponding 3-*methoxy*-1-*methyl*-4-iso*propylbenzene* (*p*-thymyl methyl ether), D^0 0·9554, $D^{14\cdot8}$ 0·9435, $n_D^{14\cdot8}$ 1·50873, and b. p. 213—214°/760 mm., a

colourless mobile liquid of characteristic odour. On demethylation it yields 3-*hydroxy*-1-*methyl*-4-iso*propylbenzene* (*p*-thymol), D^{0} 0·9954, $D^{17.8}$ 0·9817, $n_D^{17.8}$ 1·52438, b. p. 228—229°/760 mm. (corr.), m. p. 36°, which is less pungent and more soluble in water than ordinary thymol, and gives no coloration with ferric chloride. Dissolved in acetic acid it gives with sulphuric acid a yellow coloration, whilst the two isomerides give gooseberry-red colorations under these conditions. With chloro-acetic acid in presence of sodium hydroxide, it forms p-*thymyl*-3-*oxy-acetic acid*, m. p. 131·5°, which occurs in felted masses of crystals, and is slightly soluble in cold water, more so on warming. T. A. H.

Anthranolsulphonic Acids. CARL LIEBERMANN and M. ZSUFFA (*Ber.*, 1910, **43**, 1007—1012).—The sodium and potassium salts of the sulphonic acids derived from anthraquinone and its hydroxy-compounds can be reduced by means of tin and concentrated hydrochloric acid in presence of glacial acetic acid to the corresponding sulphonic acids of anthranol and its hydroxy-derivatives. The salts of these reduction products can be readily obtained in a pure form when much acetic acid and only a small amount of concentrated hydrochloric acid is used; otherwise the products are mixtures of the sulphonic acids, their salts, and alkali chlorides, and the separation is tedious. In certain cases it is not necessary to use hydrochloric acid at all. When the tin is precipitated as sulphide, the greater portion of the sulphonate is carried down at the same time, and can be extracted by means of hot water. The solution is then evaporated under reduced pressure, and the salt crystallises on cooling.

Potassium anthranol-1-*sulphonate*, $C_6H_4<\overset{CH}{\underset{C(OH)}{|}}>C_6H_3\cdot SO_3K$, forms pale yellow plates, and its aqueous solution when made alkaline turns pale orange colour.

Potassium anthranol-1 : 8-*disulphonate*,

$$SO_3K\cdot C_6H_3<\overset{CH}{\underset{C(OH)}{|}}>C_6H_3\cdot SO_3K,$$

forms lemon-yellow, sparingly soluble needles, and yields a red basic potassium salt. The neutral solution yields precipitates with salts of calcium, barium, and lead.

Sodium 1 : 2-*dihydroxyanthranol*-3-*sulphonate*,

$$C_6H_4<\overset{CH}{\underset{C(OH)}{|}}>C_6H_2(OH)_2\cdot SO_3Na,$$

obtained by reducing sodium alizarinsulphonate, is a brilliant yellow salt, and when moist turns brown on exposure to the air. The corresponding *acid*, $C_{14}H_{10}O_6S$, forms pale yellow needles, and is readily soluble.

Sodium 1 : 2 : 6-*trihydroxyanthranolsulphonate*, $C_{14}H_5(OH)_4\cdot SO_3Na$, resembles the 1 : 2-dihydroxy-derivative.

Sodium 1 : 2 : 7-*trihydroxyanthranolsulphonate* crystallises with $2.5H_2O$, which it loses at 110°. The *barium* salt is sparingly soluble. J. J. S.

Nitroquinol Monomethyl Ether. HUGO KAUFFMANN and IMMANUEL FRITZ (*Ber.*, 1910, **43**, 1214—1218).—By the hydrolysis of

nitroquinol dimethyl ether, a monomethyl ether was obtained (Abstr., 1907, i, 127), which presented some points of difference from the monomethyl ether described by Weselsky and Benedikt (Abstr., 1881, 1139). It is now shown that both substances are the same.

It would appear that in the dimethyl ether the methoxyl in the ortho-position to the nitro-group is more easily hydrolysed than that in the meta-position. To prove this, it is necessary to show that, on nitration of quinol monoethyl ether, the nitro-group enters into the ortho-position to the free hydroxyl group. Quinol monomethyl ether was coupled with diazotised sulphanilic acid, the dye so formed converted into the benzoyl derivative, and this reduced to *benzoylaminoquinol monomethyl ether*, $OH\cdot C_6H_3(OMe)\cdot NH\cdot COPh$. The group $NH\cdot COPh$ is here ortho to hydroxyl, as when coupled with quinol monomethyl ether only an ortho-oxyazo-dye is obtained. The same product is obtained on reducing nitroquinol monomethyl ether benzoate.

Nitroquinol monomethyl ether, prepared either by hydrolysis of the dimethyl ether by means of potassium hydroxide dissolved in a mixture of alcohol or water or by the method of Weselsky and Benedikt (*loc. cit.*), forms orange-red crystals, m. p. 80°; the *benzoate* crystallises in lustrous, silky, colourless needles, m. p. 89°.

By the action of nitrous acid on quinol monomethyl ether, *p*-benzoquinone is obtained.

Sodium quinolmonomethyl-ether-azobenzenesulphonate is a red dye; the *benzoate*, prepared by the action of benzoyl chloride in presence of sodium carbonate, forms lustrous, orange-yellow plates, which sinter at 240°, m. p. 260—270° (decomp.).

When reduced with iron and acetic acid, *benzoylaminoquinol monomethyl ether* is obtained as colourless, flat needles, m. p. 160°. The same product is formed on reduction of nitroquinol monomethyl ether benzoate.

The thiocarbamide of aminoquinol dimethyl ether has m. p. 137°, and not 109° as stated by Baessler (Abstr., 1884, 1329). Concentrated hydrochloric acid converts it into 2:5-*dimethoxyphenylthiocarbamide*, b. p. 178—180°/16 mm., m. p. 33°. The crystals are almost colourless and do not fluoresce. E. F. A.

Action of Triphenylmethyl on Quinones. JULIUS SCHMIDLIN, JULIUS WOHL, and HANS THOMMEN (*Ber.*, 1910, **43**, 1298—1303).—Triphenylmethyl readily combines with *p*-benzoquinone, yielding *quinol triphenylmethyl ether*, $C_6H_4(O\cdot CPh_3)_2$, which crystallises in colourless, slender, glistening needles, m. p. 241° (corr.). When heated slightly above its m. p., it turns yellowish-red, but becomes colourless again when cold. When heated for some time above its m. p., the theoretical amount of benzoquinone sublimes. It dissolves in concentrated sulphuric acid, yielding quinol and triphenylcarbinol. The ether is apparently not the first product of the reaction, as a benzene solution of triphenylmethyl turns orange-red on the addition of benzoquinone, but this colour rapidly disappears and the colourless ether is deposited.

The simplest method of obtaining the ether is to shake a benzene

solution of *p*-benzoquinone and triphenylchloromethane with zinc dust during twenty-four hours. It can also be obtained by the action of the β-modification of magnesium triphenylmethyl chloride on a benzene solution of benzoquinone.

Similar products have not been obtained by using toluquinone, *o*-benzoquinone, or α-naphthaquinone. β-Naphthaquinone gave Stenhouse and Groves' dinaphthyldiquinhydrone (Trans., 1878, **33**, 417).

J. J. S.

Preparation of Hexamethylenetetraminetriguaiacol. F. HOFFMANN—LA ROCHE & Co. (D.R.-P. 220267).—*Hexamethylenetetraminetriguaiacol*, $C_6H_{12}N_4,3C_6H_4(OH)\cdot OMe$, is prepared by heating a concentrated aqueous solution of hexamethylenetetramine with guaiacol, or by treating an ammoniacal solution of guaiacol with formaldehyde; the new compound separates from the cooled reaction mixture in long needles, m. p. 80—95°. Boiling with water sets free guaiacol, a reaction which renders this compound a convenient method of keeping guaiacol (m. p. 28°) in a solid condition in tropical climates where the vapour is employed therapeutically.

F. M. G. M.

Reduction of Methyl Pulegenate. HANS RUPE and J. BÜRGIN (*Ber.*, 1910, **43**, 1228—1230).—In continuation of experiments to prepare a high rotatory, optically active primary alcohol (Abstr., 1909, i, 927), methyl pulegenate has been reduced by means of sodium ethoxide to primary *pulegyl alcohol*, $\begin{matrix}CH_2\text{—}CHMe\\ | \\ CH_2\cdot C(CMe_2)\end{matrix}\!\!>\!CH\cdot CH_2\cdot OH$, a viscid, colourless oil, b. p. 105°/10·5 mm., D^{20} 0·9296, n_D^{20} 1·48074, α_D^{20} −1·7°. The alcohol accordingly has only a small rotatory power.

The *acetate* is a mobile, colourless oil of fruity odour, b. p. 110·5—111·5°/9·5 mm.; the *benzoate* is a colourless, viscid, odourless oil, b. p. 186·5—187·5°/9·5 mm.

E. F. A.

Action of Organomagnesium Derivatives on Trialkylacetophenones. Mlle. PAULINE LUCAS (*Compt. rend.*, 1910, **150**, 1058—1061. Compare Haller and Bauer, Abstr., 1909, i, 108, 654).—The action of magnesium methyl iodide on trimethylacetophenone leads to the formation of almost the theoretical amount of γ-*phenyl*-$\beta\beta$-*dimethylbutan*-γ-*ol*, $CMe_3\cdot CMePh\cdot OH$, a viscous liquid, b. p. 116—117°/15 mm., which, on prolonged boiling under ordinary pressure, is partially transformed into an unsaturated *hydrocarbon*, b. p. 88—90°/11 mm., for which the constitution $CMe_3\cdot CPh{:}CH_2$ is suggested.

Magnesium phenyl bromide acts on trimethylacetophenone to give $\gamma\gamma$-*diphenyl*-$\beta\beta$-*dimethylpropan*-γ-*ol*, $CMe_3\cdot CPh_2\cdot OH$, b. p. 179—180°/11 mm.; on boiling at the ordinary pressure this loses water, forming an unsaturated *hydrocarbon*, $C_{17}H_{18}$, b. p. 158—159°/11 mm. Under the same conditions, magnesium benzyl chloride furnishes $\gamma\delta$-*diphenyl*-$\beta\beta$-*dimethylbutan*-γ-*ol*, b. p. 175—178°/11 mm.; the corresponding *hydrocarbon*, $C_{18}H_{20}$, has b. p. 164—165°/11 mm., and does not combine with bromine.

Trimethylacetophenone undergoes reduction to γ-phenyl-$\beta\beta$-dimethyl

propan-γ-ol when treated with magnesium propyl iodide; the product was identified by means of its phenylurethane. W. O. W.

Action of Dehydrating Agents on α-Glycols. MARC TIFFENEAU (*Compt. rend.*, 1910, **150**, 1181—1184. Compare Abstr., 1907, i, 1035).—On treatment with acetic anhydride, aldehydes of the type $CHRR'\cdot CHO$ give diacetates instead of the expected vinyl acetates. These may be obtained, however, from substituted α-glycols of the type $OH\cdot CRR'\cdot CH_2\cdot OH$; thus, for example, when estragole glycol is heated for twelve hours with acetic anhydride, a 40% yield of β-anisyl-β-methylvinyl acetate is produced.

The author declines to admit that the compound obtained by the dehydration of anethole glycol is β-*p*-methoxyphenylpropaldehyde, as stated by Balbiano (Abstr., 1908, i, 901), and adheres to his earlier view (Abstr., 1907, i, 701) that it is identical with anisylacetone. W. O. W.

Isomerism of Some Δ^{γ}-Acetylenic Glycols. GEORGES DUPONT (*Compt. rend.*, 1910, **150**, 1121—1123. Compare this vol., i, 85).—The author has discovered fresh instances of isomerism amongst glycols of the type $OH\cdot CRR'\!:\!C\cdot CRR'\cdot OH$, a number of which have been described by Iotsitch (*J. Russ. Phys. Chem. Soc.*, 1902, **33**, 242; 1903, **35**, 1269; 1906, **38**, 656). The glycol, *ααα*ζζζ*-hexachloro-Δ^{γ}-hexinene-βε-diol*, $CCl_3\cdot CH(OH)\cdot C\!:\!C\cdot CH(OH)\cdot CCl_3$, has been separated by fractional crystallisation from carbon tetrachloride into two isomeric glycols, the less soluble, crystallising in silky needles, m. p. 135°, forms a *diacetate*, m. p. 66—67°, and a *dibenzoate*, m. p. 110—112°, whilst the more soluble isomeride, m. p. 117·5—118°, yields a *diacetate*, m. p. 54—55°, and a *dibenzoate*, m. p. 95—96°. The glycol, *αδ-diphenyl-Δ^{β}-butinene-αδ-diol*, $OH\cdot CHPh\cdot C\!:\!C\cdot CHPh\cdot OH$, similarly exists in two forms; the first, m. p. 142°, is insoluble in ether, forms a *diacetate*, m. p. 88°, and on treatment with bromine furnishes a pasty mass and small quantities of crystals, m. p. 172°; the isomeride, m. p. 103—104°, is soluble in ether, and yields a *diacetate*, m. p. 56—57°, and a *dibromide*, m. p. 182°. The glycol, *βε-diphenyl-Δ^{γ}-hexinene-βε-diol*, $OH\cdot CMePh\cdot C\!:\!C\cdot CMePh\cdot OH$, is separable by ether into two compounds; the less soluble has m. p. 163°, whilst the isomeride has m. p. 125—127°; the corresponding *dibromides* have m. p. 124° and 125—127° respectively. W. O. W.

Preparation of Arylsulphoxidoacetic Acids. FARBENWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 221261. Compare this vol., i, 320).—The oxidation of arylthioglycol-*o*-carboxylic acids with sodium hypochlorite, also with potassium permanganate, has previously been described.

o-*Chlorophenylsulphoxidoacetic acid*, colourless needles, is obtained when a cold alkaline solution of *o*-chlorophenylthioglycollic acid is treated with chlorine.

p-*Chloro*-o-*tolylsulphoxidoacetic acid* is analogously prepared, and forms colourless needles. F. M. G. M.

*α-cyclo*Geranic **Derivatives. I.** LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1910, [iv], 7, 350—354).—Barbier and Bouveault have shown previously (Abstr., 1897, i, 537) that *cyclo*geranionitrile on hydrolysis furnishes a mixture of two isomeric amides, m. p. 121° and 202° respectively, which cannot be converted into their corresponding acids. It is now shown that the amide, m. p. 121°, corresponds with *α-cyclo*geranic acid, and that the second amide is probably that corresponding with the *β*-acid.

*α-cyclo*Geranic acid was prepared by condensing methylheptenone with ethyl iodoacetate, in presence of zinc and isomerising directly the ethyl geraniate obtained to ethyl *cyclo*geraniate, b. p. 101—102°/10 mm., which was probably a mixture of the *α*- and *β-cyclo*-esters. This was hydrolysed by alcoholic potash at 110—120°, and the acid liberated. The portion which crystallised was collected, and the mother liquors were extracted with ether. The acid so obtained was distilled under reduced pressure and then recrystallised from light petroleum, and yielded pure *α-cyclo*geranic acid, m. p. 106°. This was esterified by heating it with ethyl bromide and sodium ethoxide in alcohol at 120° in a closed vessel. Ethyl *α-cyclo*geraniate, b. p. 101—102°/10 mm., is a colourless liquid, which is saponified with difficulty, yielding pure *α-cyclo*geranic acid. The acid was converted into the chloride by treatment with phosphorus pentachloride, and this on solution in ether and saturation with dry ammonia furnished *α-cyclo*geraniamide, m. p. 120—121°, identical with that obtained from geranionitrile (see above). It is probable therefore that the second amide, m. p. 202°, is *β-cyclo*geraniamide. T. A. H.

*α-cyclo*Geraniol. II. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1910, [iv], 7, 354—357).—Ethyl *α-cyclo*geraniate, prepared as described in the preceding abstract, is not reduced by long-continued treatment with sodium in alcohol, indicating that its ethylene linking is in the *βγ*-position. *α*-cyclo*Geranyl acetate*, b. p. 115°/20 mm., obtained by the action of acetic anhydride at 100°, is a colourless liquid. The alcohol also yields a *phenylurethane*, m. p. 75°, which crystallises in colourless needles. When heated with pyruvic acid at 120—140°, *α-cyclo*geraniol furnishes a *substance*, $C_{13}H_{20}O_2$, b. p. 180°/10 mm., m. p. 114°, which crystallises from hot alcohol or a mixture of ether and light petroleum in splendid colourless tablets. It forms crystalline salts with alkalis, but does not combine with bromine or react with hydroxylamine or acetic anhydride. It is possible that a true pyruvate is first formed, and that then a molecule of water becomes attached to the ethylene linking and provokes the formation of a saturated closed-chain with the other end of the pyruvic acid molecule. The formation of this substance is a useful means of identifying *α-cyclo*geraniol. The amide, m. p. 121°, obtained by the hydrolysis of geranionitrile (Abstr., 1897, i, 537), on reduction with sodium in amyl alcohol (Abstr., 1904, i, 213) furnishes *α-cyclo*geraniol, and thus provides further evidence of the derivation of this amide from *α-cyclo*geranic acid (compare preceding abstract).

Commercial *cyclo*geraniol, prepared by the cyclic isomerisation of geranyl acetate, is not homogeneous; it contains *α-cyclo*geraniol, which

was identified by means of the pyruvic acid compound described above, and an isomeric alcohol, yielding a true pyruvate. T. A. H.

Synthesis of *m*-Bromobenzoic Anhydride. NEGOITA DANAÏLA (*Bull. Soc. chim.*, 1910, [iv], 7, 286—288).—*m-Bromobenzoic anhydride*, m. p. 148—149°, is prepared by heating at 150—200° during two and a-half hours a mixture of sodium *m*-bromobenzoate and *m*-bromobenzoyl chloride; it is best purified by sublimation, and then crystallises in long, colourless filaments. The anhydride is soluble in chloroform or benzene, and slightly so in ether or light petroleum. T. A. H.

Preparation of *iso*Butyl *p*-Aminobenzoate. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 218389. Compare Abstr., 1909, i, 921).—When *p*-aminobenzoic acid is boiled with *iso*butyl alcohol or iodide, products of therapeutic value as anæsthetics are obtained.

iso*Butyl* p-*aminobenzoate*, colourless needles, m. p. 65°, is prepared by saturating an *iso*butyl-alcoholic solution of the amino-acid with hydrogen chloride at 100°, and isolating the product by the insolubility of its hydrochloride in ether.

iso*Butyl* p-*nitrobenzoate*, yellow needles, m. p. 70°, is similarly prepared from *p*-nitrobenzoic acid; on reduction with aluminium and moist ether, the foregoing compound is obtained. iso*Butyl* p-*β-naphtholazobenzoate*, $C_4H_9 \cdot CO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, m. p. 157—158°, is prepared by the esterification of *p*-*β*-naphtholazobenzoic acid. The solubility of these esters in water is stated in the patent. F. M. G. M.

Alkylation of Aromatic Amino-acids. II. 5-Iodo-2-aminobenzoic Acid and 3 : 5-Di-iodo-2-aminobenzoic Acid. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1910, 43, 398—411). —When the salts of *o*-, *m*-, and *p*-aminobenzoic acids are treated with alkyl halides, alkylaminobenzoic acids are produced, but esters of the type $NH_2 \cdot C_6H_4 \cdot CO_2R$ do not seem to be formed. Certain derivatives of the aminobenzoic acids, however, do yield esters of this type, in which the alkyl radicle does not enter the amino-group, and from which the acid can be recovered by hydrolysis. This is the case with the salts of 3 : 5-di-iodo-4-aminobenzoic acid, 3 : 5-dinitro-4-aminobenzoic acid, and 3-nitro-2-aminobenzoic acid, in each of which the substituting atoms or groups are adjacent to the amino-group. 3-Nitro-5-aminobenzoic acid, on the other hand, yields an *N*-alkyl derivative.

It has now been found that 5-iodo-2-aminobenzoic acid gives an *N*-alkyl derivative, whilst 3 : 5-di-iodo-2-aminobenzoic acid yields an ester, the adjacent substituents in this case being CO_2H and I. When potassium 5-iodo-2-aminobenzoate is heated with ethyl iodide, 5-*iodo*-2-*ethylaminobenzoic acid*, m. p. 162° (decomp.), is obtained, which forms minute prisms.

2 : 5-*Di-iodobenzoic acid*, m. p. 183°, obtained by the action of potassium iodide on the product of the diazotisation of 5-iodo-2-aminobenzoic acid, crystallises in slender prisms; its *sodium* salt is described. The *ethyl* ester, m. p. 65°, forms colourless, silky needles.

3 : 5-*Di-iodo-2-aminobenzoic acid*, $NH_2 \cdot C_6H_2I_2 \cdot CO_2H$, m. p. 230—232° (decomp.), obtained by the action of iodine monochloride on a solution

of 5-iodo-2-aminobenzoic acid in dilute hydrochloric acid, crystallises in slender prisms; the *chloride* and the *ammonium* and *sodium* salts have been prepared. The *amide*, m. p. 238—239° (decomp.), forms long needles, and the *ethyl* ester, m. p. 101°, slender prisms. When the product of the diazotisation of this acid is treated with potassium iodide, 2:3:5-*tri-iodobenzoic acid*, m. p. 224—226°, is produced, which forms colourless, slender prisms; the *sodium* salt is described. 3:5-*Di-iodo-2-aminothiolbenzoic acid*, $NH_2 \cdot C_6H_2I_2 \cdot CO \cdot SH$, m. p. 116° (decomp.), obtained by the action of potassium sulphide on 3:5-di-iodo-2-aminobenzoyl chloride, forms a red, crystalline powder. When this substance is heated in chloroform solution, it is converted into 3:5-*di-iodo-2-aminobenzoyl disulphide*, $(NH_2 \cdot C_6H_2I_2 \cdot CO)_2S_2$, which forms a yellow powder and decomposes at 202°. 3:5-*Di-iodo-2-aminobenzanilide*, m. p. 224° (decomp.), obtained by heating the disulphide with aniline, crystallises in slender prisms. E. G.

Preparation of Halogen Derivatives of Phenylglycine-*o*-carboxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 220839. Compare this vol., i, 318, 319).—The preparation and constitution of nitrogen derivatives of phenylglycine-*o*-carboxylic acids and of anthranilodi-ω-acetic acids have previously been recorded; further work is now described in which halogenated anthranilic acids are employed for the same condensation.

When 4:6-dichloroanthranilic acid (m. p. 222—224°) is treated with formaldehyde, a condensation product, needles, m. p. 170°, is obtained, which on subsequent treatment with potassium cyanide yields 3:5-*dichloro-ω-cyanomethylanthranilic acid*, colourless needles, m. p. 157—158°, and on subsequent hydrolysis with sodium hydroxide gives 4:6-dichlorophenylglycine-2-carboxylic acid, identical with that prepared by chlorinating phenylglycine-*o*-carboxylic acid.

Dibromophenylglycine-o-carboxylic acid, needles, m. p. 245—248°, is prepared in a similar manner from dibromoanthranilic acid (m. p. 225°); the *formaldehyde* product forms needles, m. p. 184—185°; and *dibromo ω-cyanomethylanthranilic acid* crystallises in prisms, m. p. 185—190°.

Tetrachlorophenylglycine-o-carboxylic acid crystallises from hot water in colourless needles, m. p. 198°; the *formaldehyde* product has m. p. 216°; and *tetrachloro-ω-cyanomethylanthranilic acid* forms minute crystals, m. p. 178°.

The *tetrachloroanthranilic acid* required for the above condensation was obtained from tetrachlorophthalic anhydride by heating with ammonium hydroxide and subsequently treating with sodium hypochlorite; it crystallises from water in slender needles, m. p. 182°; the *calcium* salt forms leaflets; the *barium* salt, needles. F. M. G. M.

New Synthesis of Benzoylenecarbamide. HERMANN FINGER and W. ZEH (*J. pr. Chem.*, 1910, [ii], 81, 466—470).—*Ethyl cyano-anilide-o-carboxylate*, $CN \cdot NH \cdot C_6H_4 \cdot CO_2Et$, m. p. 176°, obtained by heating ethyl cyanoimidocarbonate and methyl or ethyl anthranilate in the presence of a little cuprous chloride as catalyst, separates from paraldehyde in colourless needles; the *hydrochloride* or the

hydriodide at 200° yields ethyl chloride or iodide and benzoylene-carbamide, which is also produced when the hydrochloride is heated with alcohol or glacial acetic acid, or when the ester itself is heated with hydrochloric or moderately concentrated sulphuric acid.

C. S.

Alkylation of Ethyl Cyanoanilide-*o*-carboxylate. HERMANN FINGER (*J. pr. Chem.*, 1910, [ii], **81**, 470—472).—The treatment of a warm alcoholic solution of ethyl cyanoanilide-*o*-carboxylate (preceding abstract) with sodium ethoxide and methyl sulphate leads to the formation of o-*carbethoxyphenylmethylcarbodi-imide*,

$$NMe\!:\!C\!:\!N\cdot C_6H_4\cdot CO_2Et,$$

m. p. 77·5°, the constitution of which follows from the fact that the *hydrochloride*, $C_{11}H_{12}O_2N_2,HCl$, yields γ-methylbenzoylenecarbamide, m. p. 237·5°, when heated at 100°, or when kept in chloroform for a short time at the ordinary temperature.

C. S.

Transformation of Synthetical and Hetero-cinnamic Acids into Storax Acid. EMIL ERLENMEYER and G. HILGENDORFF (*Ber.*, 1910, **43**, 1076—1078. Compare this vol., i, 175; Riiber and Goldschmidt, *ibid.*, 174).—When pure synthetical cinnamic acid or the hetero-acid is boiled with water and animal charcoal, pure storax acid is obtained. There is a loss of some 10% of the original acid, but according to the authors the change cannot be due to the removal of some impurity (substituted cinnamic acids) by the charcoal, as when a mixture of storax acid and a substituted cinnamic acid is boiled with water and charcoal, the substituted acid is not removed. The change is probably due to a molecular rearrangement of some type.

Repeated solution of the hetero-acid in dilute sodium carbonate and precipitation with hydrochloric acid produces a gradual change.

When benzaldehyde and acetic anhydride are heated in a sealed tube at 170° for ten hours and subsequently condensed with sodium acetate, the product is storax-cinnamic acid.

J. J. S.

Phenylglyceric Acid and Phenylpyruvic Acid. WALTER DIECKMANN (*Ber.*, 1910, **43**, 1032—1035).—α-Oxy-$\beta\gamma$-diphenylbutyrolactone (compare this vol., i, 385) is formed when phenylglyceric acid (either isomeride) and benzaldehyde are boiled with glacial acetic and hydrochloric acids. As the lactone is formed by the condensation of benzaldehyde with phenylpyruvic acid, it appeared probable that its formation from phenylglyceric acid was due to the intermediate production of phenylpyruvic acid.

It is now shown that phenylpyruvic acid is formed when the glyceric acid is heated with 20—50% sulphuric acid, or with concentrated hydrochloric acid. The reaction consists in the elimination of water and the molecular rearrangement of the resulting α-hydroxy-cinnamic acid into phenylpyruvic acid:

$$OH\cdot CHPh\cdot CH(OH)\cdot CO_2H \longrightarrow CHPh\!:\!C(OH)\cdot CO_2H \longrightarrow CH_2Ph\cdot CO\cdot CO_2H.$$

When phenylglyceric acid is boiled for some time with acetic anhydride, it yields *α-acetoxycinnamic acid*, $CHPh:C(OAc)\cdot CO_2H$, m. p. 169—171°, which on hydrolysis gives acetic and phenylpyruvic acids. The same acetyl compound is formed when phenylpyruvic acid is boiled with acetic anhydride.

The *diacetyl* derivative of phenylglyceric acid (m. p. 141°) is formed by acetylating the acid with acetic anhydride and a few drops of concentrated sulphuric acid. It crystallises in colourless plates, m. p. 88—90°. J. J. S.

Phenylglycidic Acid. WALTER DIECKMANN (*Ber.*, 1910, **43**, 1035—1038. Compare Erlenmeyer, Abstr., 1880, 472).—Phenylglycidic acid is not as unstable as stated by Erlenmeyer. It can be obtained by the elimination of halogen hydride from phenyl-α-chloro- or α-bromo-lactic acid, or by the hydrolysis of its ester, and is identical with the compound described by Erdmann (D.R.-P. 107228) as the β-lactone of phenylglyceric acid. Its strongly acidic properties point to the glycide constitution $O<\begin{matrix}CHPh\\ |\\ CH\cdot CO_2H\end{matrix}$ rather than to the lactone formula. It crystallises in colourless plates, m. p. 83—84°, and at the same time evolves carbon dioxide and yields phenylacetaldehyde.

The *normal potassium* salt, $C_9H_7O_3K$, forms anhydrous crystals; the *acid potassium* salt, $KH(C_9H_7O_3)_2,2H_2O$, is very sparingly soluble. J. J. S.

l-Hydroxyphenyl-lactic Acid and its Occurrence in the Urine of Dogs Suffering from Phosphorus Poisoning. YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, **65**, 397—401).—l-*Hydroxyphenyl-lactic acid*, $C_9H_{10}O_4,\frac{1}{2}H_2O$, obtained by mixing a solution of tyrosine in sulphuric acid with an aqueous solution of barium nitrite, keeping overnight, filtering, and precipitating with lead acetate, crystallises in long needles, m. p. 162—164° and $[\alpha]_D$ −18°. The *calcium* salt crystallises with $4\cdot 5H_2O$.

The acid appears to be identical with the product obtained by Blendermann (Abstr., 1883, 876) from the urine of rabbits fed with tyrosine.

The *l*-acid is present in the urine of dogs poisoned with phosphorus. J. J. S.

Synthesis of p-Hydroxymandelic Acid and its Occurrence in the Urine in Cases of Acute Yellow Atrophy of the Liver. ALEXANDER ELLINGER and YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, **65**, 402—413).—*p*-Hydroxymandelic acid has been synthesised from *p*-methoxyacetophenone by the following series of reactions: (1) $OMe\cdot C_6H_4\cdot CO\cdot CH_3 + 3O = OMe\cdot C_6H_4\cdot CO\cdot CO_2H + H_2O$; (2) $OMe\cdot C_6H_4\cdot CO\cdot CO_2H + H_2O = MeOH + OH\cdot C_6H_4\cdot CO\cdot CO_2H$ (compare Bouveault, *Bull. Soc. chim.*, 1897, [iii], **17**, 948);

$$(3)\ OH\cdot C_6H_4\cdot CO\cdot CO_2H + 2H = OH\cdot C_6H_4\cdot CH(OH)\cdot CO_2H,$$

and the racemic acid has been resolved by means of its cinchonine salt. The active acid thus obtained differs completely from the acid isolated by Schulzen and Riess, in 1869, from the urine of patients

suffering from acute yellow atrophy of the liver, and stated to be *p*-hydroxymandelic acid.

A small amount of a by-product, $C_8H_8O_3$, is obtained in the hydrolysis of *p*-methoxyphenylglyoxylic acid. It is probably a hydroxytoluic acid.

p-*Hydroxymandelic acid*, $OH\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, crystallises in microscopic plates containing $1H_2O$ and melting at 80—90°. When anhydrous it has m. p. 105—106°.

The *d*-acid crystallises in large plates, contains $1H_2O$, has m. p. 103—104° when anhydrous, and $[\alpha]_D$ +144·4°.

The *cinchonine* salt of the *l*-acid is sparingly soluble, and crystallises in brilliant prisms; the *l*-acid contains $\frac{1}{2}H_2O$. The *calcium* salt, $Ca(C_8H_7O_4)_2,5\frac{1}{2}H_2O$, crystallises in brilliant plates.

Optically active acids could not be detected in the urine of animals to which *p*-hydroxyphenylglyoxylic acid was administered; similar results were obtained when *dl*-hydroxymandelic acid was used.

J. J. S.

Action of Ethyl Diazoacetate on Benzaldehyde. WALTER DIECKMANN (*Ber.*, 1910, **43**, 1024—1031).—The product obtained by Buchner and Curtius (Abstr., 1885, 1238) by the action of ethyl diazoacetate on benzaldehyde, and regarded as benzylidene*bis*benzoylacetic ester, is shown to be ethyl benzylidenedioxyphenylpropionate, $CHPh<\begin{matrix}O\cdot CHPh\\ O\cdot CH\cdot CO_2Et\end{matrix}$. The sodium salt, methyl ester, and acid are also the corresponding derivatives of benzylidenedioxyphenylpropionic acid. The m. p. of the acid is 132°, not 130°. When warmed with acetic acid or with aqueous alcohol it is completely hydrolysed to benzaldehyde and phenylglyceric acid (m. p. 121°). When the acid or its ethyl ester is boiled for fifteen hours with an excess of acetic and hydrochloric acids, carbon dioxide is evolved and α-oxy-$\beta\gamma$-diphenylbutyrolactone is formed (Erlenmeyer and Knight, Abstr., 1894, i, 592; Erlenmeyer and Lux, *ibid.*, 1898, i, 668).

In the preparation of the ester from benzaldehyde and ethyl diazoacetate, an *isomeride* of the ester $C_{18}H_{18}O_4$ is obtained. This crystallises in glistening, colourless prisms, m. p. 61—62°, and is much more readily soluble than the ester, m. p. 103—104°, in all solvents. It yields α-oxy-$\beta\gamma$-diphenylbutyrolactone when boiled with glacial acetic and hydrochloric acids.

The corresponding *acid*, $C_{16}H_{14}O_4$, crystallises in microscopic prisms, m. p. 156°, and when its aqueous alcoholic solution is boiled, the acid yields benzaldehyde and phenylglyceric acid (m. p. 141°). The same acid is formed when a mixture of benzaldehyde and phenylglyceric acid is shaken for several hours with five times its weight of 50% sulphuric acid.

The formation of the ester is represented by the following reactions:

$$Ph\cdot CHO + N_2{:}CH\cdot CO_2Et \longrightarrow \begin{matrix}CHPh\text{——}O\\ |\qquad\qquad\\ CH(CO_2Et)\cdot N\end{matrix}\!\!>\!N\,;\ \begin{matrix}CHPh\text{——}O\\ |\qquad\qquad\\ CH(CO_2Et)\cdot N\end{matrix}\!\!>\!N + Ph\cdot CHO \longrightarrow N_2 + \begin{matrix}CHPh\text{——}O\\ |\qquad\qquad\\ CH(CO_2Et)\cdot O\end{matrix}\!\!>\!CHPh.$$

J. J. S.

Preparation of Crystalline Salicylosalicylic [o-Salicyloxybenzoic] Acids. C. F. BOEHRINGER and SÖHNE (D.R.-P. 220941. Compare Abstr., 1909, i, 803).—It is found that the ethers of o-salicyloxybenzoic acid are readily hydrolysed to the parent acid.

Acetylsalicylosalicylic [2-o′-*acetoxybenzoyloxybenzoic*] *acid*,

$$AcO\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 159°, is prepared by condensing molecular equivalents of salicylic and o-acetoxybenzoic acids with phosphorus trichloride in the presence of dimethylaniline; by treatment with sodium hydroxide at the ordinary temperature, the acetyl group is removed, yielding salicylosalicylic acid.

Ethylcarbonylsalicylosalicylic (2-o-*ethylcarbonatobenzoyloxybenzoic*) *acid*, m. p. 122°, obtained by the condensation of molecular proportions of ethylcarbonatobenzoylbenzoic and salicylic acids, undergoes similar hydrolysis on treatment with ammonium hydroxide.

Benzylsalicylosalicylic [2-o-*benzyloxybenzoyloxybenzoic*] *acid*,

$$CH_2Ph\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 124°, is prepared as follows: o-benzyloxybenzoic acid is heated during half an hour with phosphorus trichloride in carbon tetrachloride, extracted with cold sodium hydroxide, the oily portion dried, and the solvent removed by distillation in a vacuum. The residual o-*benzyloxybenzoyl chloride* (a dark oil) is then treated with an equal weight of disodium salicylate and boiled in benzene solution; the mixture is extracted with sodium carbonate, acidified, and again extracted with benzene, when the product is obtained as a syrup which subsequently solidifies. F. M. G. M.

Preparation of Salicylic Esters of Dihydroxyalkylaliphatic Acid Esters. LES ETABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 221262).—When the esters of halogenalkylhydroxy-aliphatic acids of the general formula:

$$CH_2X\cdot CR(OH)\cdot CO_2R'$$

(X = halogen, R and R′ = alkyl) are heated with salicylic acid or its salts, compounds of the type $OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CR(OH)\cdot CO_2R$ and of great therapeutic value are obtained.

*Ethyl β-salicyloxy-α-hydroxy*iso*butyrate*,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CMe(OH)\cdot CO_2Et,$$

m. p. 51—52°, is prepared by heating sodium salicylate with ethyl β-chloro-α-hydroxy*iso*butyrate at 180—185°; it is insoluble in water, but dissolves in sodium hydroxide, by which it is slowly decomposed.

*Propyl β-salicyloxy-α-hydroxy*iso*butyrate*,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CMe(OH)\cdot CO_2\cdot C_3H_7,$$

is analogously prepared, but in this case it is advisable to employ some reduced copper and potassium iodide as catalysts and heat at a temperature of 260—280°; it is an odourless syrup, b. p. 203°/15 mm., very sparingly soluble in water.

The iso*amyl* ester, b. p. 200°/11 mm., has a powerful odour, and is insoluble in water. F. M. G. M.

New Cyclic Compounds from Ethyl Dicarboxyglutaconate. MAX GUTHZEIT and ERICH HARTMANN (*J. pr. Chem.*, 1910, [ii], 81, 329—381).—*Ethyl α-chlorodicarboxyglutaconate*,

$$C(CO_2Et)_2{:}CH\cdot CCl(CO_2Et)_2,$$

obtained by the action at the ordinary temperature of chlorine on ethyl dicarboxyglutaconate or on a chloroform solution of ethyl sodiodicarboxyglutaconate (Coutelle, Abstr., 1906, i, 139), is a colourless, odourless, mobile liquid, which does not give a coloration with ferric chloride, and is reduced by zinc and acetic acid to *ethyl dicarboxyglutarate*, b. p. 192°/12 mm. *Ethyl αβ-dibromodicarboxyglutarate*, obtained by the action at 0° of bromine in chloroform solution of the ester in intense sunlight, is a viscous liquid, which cannot be distilled and slowly evolves hydrogen bromide, forming *ethyl α-bromodicarboxyglutaconate*, which can also be prepared in a similar manner to the corresponding chloro-compound.

The first step in a series of reactions suggested for the synthesis of ethyl *cyclo*hexane-1 : 1 : 2 : 2 : 4 : 4 : 5 : 5-octacarboxylate is the action of iodine on ethyl sodiodicarboxyglutaconate. The reaction, however, does not follow the expected course: $2CNa(CO_2Et)_2 \cdot CH\colon C(CO_2Et)_2 + I_2 = 2NaI + C(CO_2Et)_2\colon CH \cdot C(CO_2Et)_2 \cdot C(CO_2Et)_2 \cdot CH\colon C(CO_2Et)_2$, but results in the formation of a saturated *ester*, $C_{30}H_{42}O_{16}$, m. p. 86°, which, in consequence of the transformations described below, is regarded as ethyl 2 : 2 : 4 : 4-tetracarboxy*dicyclo*-011-butane-1 : 3-dimalonate (Baeyer's notation):

$$CH(CO_2Et)_2 \cdot C \begin{array}{c} \diagup C(CO_2Et)_2 \diagdown \\ \overline{} \\ \diagdown C(CO_2Et)_2 \diagup \end{array} C \cdot CH(CO_2Et)_2.$$

The ester is obtained in more than 90% yield by carefully observing the following conditions. Finely powdered ethyl sodiodicarboxyglutaconate is added to a cold solution of iodine in toluene. The mixture is stirred as rapidly as possible (3000 revolutions per minute), and is then heated. The viscous liquid obtained after the removal of the toluene is mixed with a little ether, and placed in a desiccator which is rendered vacuous; after half an hour the yellow solid is collected, and recrystallised from ether by the addition of petroleum. The ester, which can also be obtained by the interaction of (i) ethyl sodiodicarboxyglutaconate and ethyl α-bromodicarboxyglutaconate in boiling xylene, (ii) the sodio-compound and ethyl α-chlorodicarboxyglutaconate in xylene at 180°, (iii) sulphur and ethyl cupridicarboxyglutaconate in boiling benzene, crystallises in stout prisms, and is unaffected by bromine, alkaline potassium permanganate, or zinc and acetic acid. Its behaviour with various reagents is quite different from that of the esters, $C_{30}H_{44}O_{16}$, m. p. 103° and 88° respectively, obtained by Guthzeit, Weiss, and Schäfer (Abstr., 1909, i, 933), which are derivatives of *cyclo*butane.

When an ethereal solution of the ester, m. p. 86°, is treated with alcoholic sodium ethoxide, and after ten minutes the mixture is added to petroleum, a tetra-sodium *derivative*, $C_{26}H_{30}O_{16}Na_4$, is precipitated as a red, amorphous powder. The acidification of an alcoholic solution of this sodium derivative yields a *hexa-ester dicarboxylic acid*,

$$CO_2H \cdot CH(CO_2Et) \cdot C \begin{array}{c} \diagup C(CO_2Et)_2 \diagdown \\ \overline{} \\ \diagdown C(CO_2Et)_2 \diagup \end{array} C \cdot CH(CO_2Et) \cdot CO_2H,$$

m. p. 193°, which forms a white, crystalline *barium* salt and a light green, amorphous *copper* salt, $C_{26}H_{32}O_{16}Cu$, and regenerates the original ester, m. p. 86°, on treatment with alcoholic hydrogen chloride.

When the ester, m. p. 86°, is heated for fifty hours with concentrated hydrochloric acid, carbon dioxide is evolved and white crystals are deposited on cooling; after evaporating the mother liquor, a viscous, brown residue is obtained (see below). The crystalline product is *ethyl* 2 : 2 : 4 : 4-*tetracarboxy*dicyclo-011-*butane*-1 : 3-*diacetic acid*,

$$CO_2H\cdot CH_2\cdot C\begin{matrix} \diagup C(CO_2Et)_2 \diagdown \\ \diagdown C(CO_2Et)_2 \diagup \end{matrix}C\cdot CH_2\cdot CO_2H,$$

m. p. 152°, which crystallises with $3H_2O$, forms a *zinc* salt, $C_{20}H_{24}O_{12}Zn$, and a *silver* salt, $C_{20}H_{24}O_{12}Ag_2$, is also obtained by heating the hexa-ester dicarboxylic acid, m. p. 193°, with concentrated hydrochloric acid and yields by esterification with alcoholic hydrogen chloride the corresponding *hexa*-ester, m. p. 71°, which is characterised by its pronounced property of crystallising. 2 : 4-*Dicarboxy*dicyclo-011-*butane*-1 : 3-*diacetic acid*, $CO_2H\cdot CH_2\cdot C\begin{matrix} \diagup CH(CO_2H) \diagdown \\ \diagdown CH(CO_2H) \diagup \end{matrix}C\cdot CH_2\cdot CO_2H$, is a hygroscopic, amorphous powder, which is obtained by hydrolysing the ester, m. p. 86°, the hexa-ester dicarboxylic acid, m. p. 193°, or the tetra-ester dicarboxylic acid, m. p. 152°, with 10% aqueous-alcoholic potassium hydroxide, or by the prolonged heating of the previously-mentioned viscous, brown residue with concentrated hydrochloric acid; the *methyl* and the *ethyl* esters, prepared from the silver salt, are viscous liquids, which instantly decolorise potassium permanganate.

The presence of two malonate groups in the ester, m. p. 86°, cannot be proved satisfactorily by alkylation, since the sodio-derivative cannot be obtained unhydrolysed, and the action of dry, amalgamated, granulated zinc and ethyl iodide on the ester results in the formation of an inseparable mixture of the di- and tetra-ethylated derivatives,

$$CEt(CO_2Et)_2\cdot C\begin{matrix} \diagup C(CO_2Et)_2 \diagdown \\ \diagdown C(CO_2Et)_2 \diagup \end{matrix}C\cdot CEt(CO_2Et)_2$$

and $CO_2Et\cdot CEt_2\cdot C\begin{matrix} \diagup C(CO_2Et)_2 \diagdown \\ \diagdown C(CO_2Et)_2 \diagup \end{matrix}C\cdot CEt_2\cdot CO_2Et$. The object in view can be attained by bromination, since the ester, m. p. 86°, in boiling carbon tetrachloride is converted by bromine in sunlight into the dibromo-*compound*, $CBr(CO_2Et)_2\cdot C\begin{matrix} \diagup C(CO_2Et)_2 \diagdown \\ \diagdown C(CO_2Et)_2 \diagup \end{matrix}C\cdot CBr(CO_2Et)_2$, from which the ester, m. p. 86°, is regenerated by zinc and acetic acid. The bromination of the ester, m. p. 86°, in boiling acetic acid in direct sunlight yields a tetrabromo-*compound*, which must have the constitution $CO_2Et\cdot CBr_2\cdot C\begin{matrix} \diagup C(CO_2Et)_2 \diagdown \\ \diagdown C(CO_2Et)_2 \diagup \end{matrix}C\cdot CBr_2\cdot CO_2Et$, since it is reduced by zinc and acetic acid to the hexa-ester, m. p. 71°. The chlorination of the ester, m. p. 86°, in boiling carbon tetrachloride in sunlight yields a viscous tetrachloro-*compound*, $C_{24}H_{30}O_{12}Cl_4$, the constitution of which is indicated by its reduction to the hexa-ester,

m. p. 71°. When the chlorination, however, is effected in the dark, an isomeric tetrachloro-*compound* is obtained, to which the constitution

$$CCl(CO_2Et)_2\cdot C\begin{cases} CCl(CO_2Et) \\ CCl(CO_2Et) \end{cases} C\cdot CCl(CO_2Et)_2$$

is ascribed. It is reduced by zinc and acetic acid to *ethyl* 2 : 4-*dicarboxy*dicyclo-011-*butane*-1 : 3-*dimalonate*,

$$CH(CO_2Et)_2\cdot C\begin{cases} CH(CO_2Et) \\ CH(CO_2Et) \end{cases} C\cdot CH(CO_2Et)_2,$$

a mobile liquid which instantly decolorises potassium permanganate, yields an amorphous tetracarboxylic *acid*, $C_{10}H_{10}O_8$, by hydrolysis with concentrated hydrochloric acid, and forms a yellow tetrasodio-*derivative*, $C_{20}H_{22}O_{12}Na_4$, the acidification of the alcoholic solution of which yields a liquid *tetra-ester dicarboxylic acid*,

$$CO_2Et\cdot CH(CO_2H)\cdot C\begin{cases} CH(CO_2Et) \\ CH(CO_2Et) \end{cases} C\cdot CH(CO_2H)\cdot CO_2Et,$$

which instantly decolorises potassium permanganate. C. S.

Simple Method for the Preparation of Large Quantities of Ellagic Acid. Hans Trunkel (*Arch. Pharm.*, 1910, **248**, 202—204).—A 1% solution of tannin is treated with sufficient 5% sodium carbonate to adjust the proportion of tannin to carbonate to 2 : 1; the mixture is exposed to the air for eight days in flat vessels with occasional stirring. The resulting sodium ellagate, after decantation of the liquor, is treated with alcohol to facilitate filtration, and is obtained in 47% yield. The acid is liberated by cold dilute hydrochloric acid, washed with alcohol, and crystallised from pyridine; yield 50%. C. S.

Tannins. III. Ellagitannic Acid. Maximillian Nierenstein (*Ber.*, 1910, **43**, 1267—1270. Compare Abstr., 1909, i, 174, and Perkin and Nierenstein, Trans., 1905, **87**, 1412).—Pure ellagitannic acid has been prepared by repeatedly treating the acid from myrobalan with alkali and ethyl chloroformate, and then decomposing with pyridine according to Fischer's method. The acid has the composition $C_{26}H_{28}O_{19},3H_2O$, crystallises from a mixture of pyridine and glacial acetic acid in pale yellow plates, m. p. 329—336°, after sintering at 300—306°, and $[\alpha]_D^{17}$ +18·02°.

When boiled with dilute sulphuric acid, it yield ellagic acid, but is not decomposed when boiled with 10% sodium carbonate solution. The acid is hydrolysed by emulsin to luteo-acid, and is thus a a glucoside of luteo-acid (*loc. cit.*), and one of the dextrose molecules is probably attached to the position 6. J. J. S.

Action of Light on Benzaldehyde in Presence of Iodine. Luigi Mascarelli (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 383—389). —The action of light on benzaldehyde in presence of iodine or iodoxybenzene or iodosobenzene yields (1) benzoic acid; (2) a *dimeric benzaldehyde*, which is a dense colourless liquid, b. p. 189—191°/18 mm.; (3) the trimeric and (4) tetrameric benzaldehydes previously

described (compare Mascarelli, Abstr., 1906, i, 962; Ciamician and Silber, Abstr., 1909, i, 306); (5) traces of hydrobenzoin; (6) stilbene, and (7) an oil, not yet characterised. The relative proportions of these products vary with the compound mixed with the aldehyde, the best yield of the oil being obtained when iodine is employed. The fact that the dimeride is not obtained by the action of light on the aldehyde alone (compare Ciamician and Silber, *loc. cit.*) indicates that its formation is due to the presence of traces of iodine liberated from iodobenzene, into which both iodoxy- and iodoso-benzene tend to become transformed: $C_6H_5IO_2 \rightarrow C_6H_5IO \rightarrow C_6H_5I$. T. H. P.

Preparation of Salts of *m*-Aminobenzaldehyde in the Presence of Anhydro-*o*-aminobenzaldehyde. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 218364).—The product obtained by reducing the crude mixture of nitrobenzaldehydes with sodium hyposulphite contains about 25% of *o*-aminobenzaldehyde; the separation of this from the meta-isomeride can be effected by treatment with an adequate quantity of hydrochloric acid, when *o*-aminobenzaldehyde is completely precipitated in the form of its anhydride,

$$NH_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot CHO,$$

the *m*-aminobenzaldehyde remaining in solution in the form of its hydrochloride to be subsequently separated by known methods. The *o*-anhydride by further treatment with acids is readily resolved into pure *o*-aminobenzaldeyhyde; the hydrochloric acid may be replaced by oxalic or sulphuric acid in this reaction. F. M. G. M.

Preparation of Nitrobenzaldehyde Sulphides. GEORG KRÄNZLEIN (D.R.-P. 219839).—Chloronitrobenzaldehydes, which contain the chlorine atom in an *o*- or *p*-position to the nitro-group, react readily with sodium thiosulphate, yielding nitrobenzaldehyde sulphides.

Nitrobenzaldehyde sulphide [*2-nitro-4-aldehydophenyl sulphide*],

$$C_{14}H_8O_6N_2S,$$

m. p. 194·5—195°, is prepared by warming 4-chloro-3-nitrobenzaldehyde dissolved in alcohol with aqueous sodium thiosulphate at 70°, when the product rapidly separates in yellow crystals; the isomeric 4-nitro-2-aldehydophenyl sulphide obtained from 2-chloro-5-nitrobenzaldehyde has m. p. 297—297·5°. F. M. G. M.

Decomposition of Piperonal on Heating with Dilute Hydrochloric Acid. W. SCHUT (*Chem. Weekblad*, 1910, **7**, 371—374. Compare Fittig and Remsen, this Journ., 1873, 1143).—The black powder obtained by Fittig and Remsen by the action of dilute hydrochloric acid on piperonal contains only 67·3% of carbon. The author attributes its formation to condensation resulting from the aldehydic nature of piperonal. He does not consider that formaldehyde is produced by the action of water, and then decomposed into carbon and water. A. J. W.

Action of Carbon Disulphide and Potassium Hydroxide on Acetophenone. C. KELBER (*Ber.*, 1910, **43**, 1252—1259).—By the interaction of acetophenone, carbon disulphide, and potassium hydroxide

at the temperature of the water-bath, a *substance*, $C_9H_8OS_2$, is formed of faintly acid nature crystallising in lustrous, golden-yellow plates, m. p. 63—64°. The *dimethyl ether* forms bright yellow needles, m. p. 93—94°; the *dibenzyl ether* crystallises in thin, yellow, glistening needles, m. p. 113°, whereas the *monobenzyl ether* forms yellow crystals, m. p. 49—50°. The *dibenzoyl* derivative forms short, yellow, refractive crystals, m. p. 113—114°. The substance forms soluble, orange-red salts with alkali hydroxides, and insoluble coloured salts with the heavy metals.

Concentrated potassium hydroxide decomposes it into benzoic acid and hydrogen sulphide, alcoholic ammonia forms ammonium thiocyanate and acetophenone, and boiling aniline gives rise to benzanilide. Aniline in the cold forms a *compound*, $C_{15}H_{13}ONS$, crystallising in aggregates of light yellow needles, m. p. 78·5°, of which the *phenacyl* derivative, $C_{15}H_{12}ONS{\cdot}CH_2{\cdot}COPh$, crystallises in bunches of faintly green needles, m. p. 160—161°. On oxidation, phenylcarbylamine, benzoic and sulphuric acids are obtained.

The constitution $C_6H_5{\cdot}CO{\cdot}CH{:}C(SH)_2$ is ascribed to the compound $C_9H_8OS_2$, although the keto-group cannot be identified by hydroxylamine or phenylhydrazine. By the action of bromine on the dimethyl-derivative, a labile red *additive* product, $COPh{\cdot}CHBr{\cdot}CBr(SMe)_2$, is first formed, from which hydrogen bromide is eliminated with formation of the stable *monobromo*-derivative, $COPh{\cdot}CBr{:}C(SMe)_2$, crystallising in lustrous, light yellow crystals, m. p. 52·5—53·5°.

Oxidation with ammonium persulphate in alkaline solution yields a *compound*, $C_{18}H_{12}O_2S_3$, crystallising in golden-yellow needles, m. p. 206—207°. E. F. A.

"Dimorphism" of Benzophenone. KARL SCHAUM (*Chem. Zeit.*, 1910, **34**, 417).—The two modifications of benzophenone in the fused state exhibit small but definite differences in their physical properties (refraction and viscosity). It is probable that the molecules of the stable α-modification change when the substance is fused into those of the β-form, the concentration of which increases with the degree and the duration of the heating. The labile crystalline modification contains varying quantities of the α- and the β-forms; when the labile form changes to the stable, all the β-molecules have been converted into α-molecules. C. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. XIII. Derivatives of *cyclo*Hexane. ELMER P. KOHLER and M. CLOYD BURNLEY (*Amer. Chem. J.*, 1910, **43**, 412—418).—Earlier work has shown that many unsaturated ketones unite with organic magnesium compounds to form both αβ- and αδ-additive products, in proportions depending on the nature of the magnesium compound as well as on that of the ketone. The mode of addition to substances containing the chain $C{:}C{\cdot}C{:}O$ is affected more by the number and arrangement of the hydrocarbon residues in the ketone than by their chemical character. The relation between the mode of addition and the nature of the magnesium compound is less easily determined, but the results obtained by the action of various magnesium compounds on styryl ethyl ketone (Abstr., 1907, i, 1052)

suggest that the mode of addition to any given ketone depends more on the chemical than the spatial character of the hydrocarbon residues contained in the magnesium compound.

The experiments now described support these conclusions. Magnesium *cyclo*hexyl bromide can be obtained in a yield of more than 95% by a modification of Freundler and Damond's method (Abstr., 1905, i, 890). It reacts with styryl methyl ketone to form *a-phenyl-a-*cyclo*hexylbutan-γ-one*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COMe$, m. p. 67°, which crystallises in colourless needles; a yield of 37·2 grams was obtained from 36·4 grams of the ketone. From 42 grams of anisylideneacetone, 44 grams of *a-anisyl-a-*cyclo*hexylbutan-γ-one*,

$$C_6H_{11}\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot COMe,$$

b. p. 218°/18 mm., were obtained as a viscous liquid. *a-Phenyl-a-*cyclo*hexylpentan-γ-one*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COEt$, m. p. 71°, obtained in a yield of 43 grams from 40 grams of styryl ethyl ketone, forms colourless needles. *Phenyl*cyclo*hexylpropiophenone*, $C_6H_{11}\cdot CHPh\cdot CH_2\cdot COPh$, m. p. 122—122·5°, obtained from phenyl styryl ketone in a yield of nearly 95%, crystallises in needles.

Styryl cyclo*hexyl ketone*, $CHPh:CH\cdot CO\cdot C_6H_{11}$, m. p. 58°, prepared by condensing methyl *cyclo*hexyl ketone with benzaldehyde, crystallises in colourless plates and unites with bromine to form a *dibromide*, m. p. 139°. This ketone reacts with magnesium ethyl bromide with production of *phenylbutyl* cyclo*hexyl ketone*, $CHPhEt\cdot CH_2\cdot CO\cdot C_6H_{11}$, b. p. 188°/16 mm. *Diphenylethyl* cyclo*hexyl ketone*,

$$CHPh_2\cdot CH_2\cdot CO\cdot C_6H_{11},$$

b. p. 250°/17 mm., m. p. 68°, obtained by the action of magnesium phenyl bromide on styryl *cyclo*hexyl ketone, forms long, colourless needles. E. G.

Preparation of Hydrocarbons, Acids, Amides, and Thiophens by the Action of Ammonium Sulphide on Fatty Aromatic Ketones. CONRAD WILLGERODT and THEODOR SCHOLTZ (*J. pr. Chem.*, 1910, [ii], **81**, 382—402).—The work is an extension of that previously recorded (Abstr., 1909, i, 716; this vol., i, 117). A copper autoclave lined with lead is used. Experiments on *p*-tolyl methyl ketone, *p*-xylyl methyl ketone, mesityl methyl ketone, *a*-naphthyl methyl ketone, phenyl ethyl ketone, and colourless solid ammonium sulphide at about 215° show that (1) reduction of ketones containing methyl and ethyl radicles to the corresponding hydrocarbons occurs; (2) the acid amide and, in much smaller amount, the acid are always formed; (3) thiophen derivatives are obtained only in the cases of phenyl methyl ketone and *p*-tolyl methyl ketone; (4) the presence of complex aliphatic and aromatic radicles in the ketone hinders the formation of thiophens.

Also, the following ketones have been heated with solid ammonium sulphide: *ψ*-Cumyl methyl ketone yields 1 : 2 : 4-trimethyl-5-ethylbenzene, 15% of *ψ*-cumylacetamide, and 7% of the acid; *ψ*-cumyl ethyl ketone yields 1 : 2 : 4-trimethyl-5-propylbenzene, 6% of *β-ψ-cumylpropionamide*, $C_6H_2Me_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, m. p. 157°, and only a trace of the *acid*, m. p. 92°; *ψ*-cumyl propyl ketone yields 6% of *γ-ψ-cumylbutyramide*, m. p. 153°, and a trace of the *acid*, m. p. 71°; *ψ*-cumyl

*iso*propyl ketone yields 0·5% of *ψ-cumyl*iso*butyramide*, m. p. 158°. *ψ-Cumyl*iso*butyl ketone*, b. p. 282°, obtained from *iso*valeryl chloride and *ψ*-cumene by the Friedel-Craft reaction (*phenylhydrazone* consists of white prisms which decompose by heating), yields practically no amide when heated with ammonium sulphide at 180°. With the last ketone, therefore, the Willgerodt reaction reaches its limit in this series of ketones (compare Willgerodt and Merk, Willgerodt and Hambrecht, *loc. cit.*).

The following ketones react with solid ammonium sulphide at 215°. *m*-Diphenylyl methyl ketone yields 20% of m-*diphenylylacetamide*, $C_6H_4Ph·CH_2·CO·NH_2$, which decomposes without melting, and only a trace of the *acid*, m. p. 146°. m-*Diphenylyl ethyl ketone*, $C_6H_4Ph·COEt$, m. p. 89°, b. p. 344°, obtained from equal molecular quantities of diphenyl and propionyl chloride by the Friedel-Craft reaction, forms an *oxime*, m. p. 159°, and a *phenylhydrazone*, m. p. 122°, and by heating with ammonium sulphide yields 6% of *β*-m-*diphenylylpropionamide*, $C_6H_4Ph·CH_2·CH_2·CO·NH_2$, m. p. 196°, and hardly a trace of the *acid*, m. p. 145°. m-*Diphenylyl propyl ketone*, m. p. 74°, b. p. 354—355°, prepared from diphenyl and butyryl chloride, forms an *oxime*, m. p. 100°, and *phenylhydrazone*, m. p. 94°, and gives a very small yield of *γ*-m-*diphenylylbutyramide*, m. p. 144° (the *acid* has m. p. 100°), with ammonium sulphide. m-*Diphenylyl* iso*propyl ketone*, m. p. 56°, b. p. 346—347°, forms an *oxime*, m. p. 54°, and *phenylhydrazone*, m. p. 99°, and does not yield an amide or acid with ammonium sulphide. m-*Diphenylyl* iso*butyl ketone*, m. p. 63°, b. p. 356° (*oxime*, m. p. 131°; *phenylhydrazone*, m. p. 102·5°), does not yield an amide or acid with ammonium sulphide at 190°. C. S.

Trialkylacetonaphthones and their Decomposition by Sodamide. V. Volmar (*Compt. rend.*, 1910, **150**, 1174—1177. Compare Haller and Bauer, Abstr., 1909, i, 108—131).—The ultimate product obtained when *α*-naphthyl methyl ketone is methylated with sodamide and methyl iodide is *α-naphthyl* tert.-*butyl ketone*, $C_{10}H_7·CO·CMe_3$, m. p. 73—74°, b. p. 183—186°/19 mm.; this compound does not form a picrate, but yields with difficulty an *oxime*, m. p. 198—199°. *β-Naphthyl* tert.-*butyl ketone*, obtained in the same way, is a faintly coloured, oily liquid, b. p. 184—186°/16 mm.; the *picrate* crystallises in yellow needles, m. p. 74—75°, whilst the *oxime*, prepared by Crismer's method, has m. p. 193—194°. *α-Naphthyl* tert.-*amyl ketone*, $C_{10}H_7·CO·CMe_2Et$, is a pale yellow oil, b. p. 185—187°/14 mm., forming an *oxime*, m. p. 171—172°; the corresponding *β*-compound has b. p. 187—189°/14 mm., and forms an *oxime*, m. p. 183—184°.

On treating the foregoing ketones with sodamide, the usual decomposition takes place, fission occurring as in the case of the phenyl naphthyl ketones studied by Lucas (Abstr., 1909, i, 488).

W. O. W.

Derivatives of Resorcinol. Hugo Kauffmann and Paul Pannwitz (*Ber.*, 1910, **43**, 1205—1213. Compare Abstr., 1905, i, 280, 773; 1909, i, 99).—2:4-Dimethoxybenzophenone, prepared by the interaction of resorcinol dimethyl ether and benzoyl chloride in

presence of aluminium chloride, is a colourless compound, m. p. 83° (compare König and von Kostanecki, 1907, i, 62). It gives a yellow coloration with concentrated sulphuric acid. The *phenylhydrazone* crystallises in yellow needles, m. p. 146°; the *oxime* was obtained in two modifications, m. p. 175° and 162°, the less fusible compound being less acid and more soluble in alcohol. A by-product of the above reaction is 2-hydroxy-4-methoxybenzophenone, crystallising in long, slender, yellow needles, m. p. 62° (compare König and Kostanecki, *loc. cit.*).

Nitro-2 : 4-dimethoxybenzophenone was obtained in almost colourless plates, m. p. 153°.

By the action of phosphorus pentachloride, dimethoxybenzophenone is converted quantitatively into the *monochloro*-derivative, which is also formed by the action of chlorine on a solution of the ketone in acetic acid; it forms colourless crystals, m. p. 144°.

Dimethoxybenzophenone in ethereal solution reacts with bromobenzene and magnesium, forming 2 : 4-*dimethoxytriphenylcarbinol*, which crystallises in colourless plates, m. p. 138°, and gives a dark red coloration with concentrated sulphuric acid. It is very readily reduced by zinc dust and acetic acid to 2 : 4-dimethoxytriphenylmethane, crystallising in colourless plates, m. p. 124°. It dissolves in concentrated sulphuric acid with a yellow coloration, and is converted by phosphorus pentachloride into a monochloro-derivative.

Aluminium chloride converts dimethoxytriphenylcarbinol into 3-*hydroxy*-9-*phenylxanthen*, $OH\cdot C_6H_3<\genfrac{}{}{0pt}{}{CHPh}{O}>C_6H_4$; this crystallises in colourless, matted needles, m. p. 196°. It is soluble in alkali, and contains only one hydroxyl group, as it forms an *acetate*, crystallising in colourless rods, m. p. 158°, and a *benzoate*, separating in long, thin prisms, m. p. 194°. All three substances are characterised by a very intense green fluorescence in concentrated sulphuric acid.

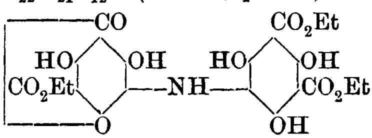
E. F. A.

Formation of Keto-asarone. VINCENZO PAOLINI (*Gazzetta*, 1910, **40**, i, 113—116).—It has been shown by Wallach and Pond (Abstr., 1896, i, 94) and by Hell and Portmann (Abstr., 1896, i, 357) that the action of alcoholic potassium hydroxide on dibromides of compounds containing a propenyl chain gives rise to ketones of the general formula R·COEt. Previous attempts to isolate in this way the ketone corresponding with dibromoasarone (compare Beckstroem, Abstr., 1904, i, 409; Széki, Abstr., 1906, i, 660) have been unsuccessful.

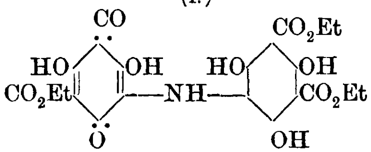
The author finds that the conditions employed by Beckstroem lead to the formation of an oil, which, when freed from bromine by the action of zinc dust and aqueous potassium hydroxide and purified by boiling with 20% sulphuric acid solution, consists of the pure *ketone*, $C_{12}H_{16}O_4$, which forms shining, white needles, softening at 106°, m. p. 108°, b. p. 186°/13 mm. This ketone is the α-ketone, R·COEt, since it yields propionic acid when heated in a sealed tube with sulphuric acid. The *semicarbazone*, $C_{13}H_{19}O_4N_3$, forms shining, white plates, m. p. 182—183°.

T. H. P.

Formation of a Keten-like Quinone and Other Completely Substituted Derivatives of Diphenylamine. Exchange of Alkyl in Esters by means of Alcoholic Ammonium Hydroxide. HERMANN LEUCHS and GEORGE THEODORESCU (*Ber.*, 1910, 43, 1239—1251. Compare Abstr., 1909, i, 106).—By the action of cold concentrated nitric acid on ethyl phloroglucinoldicarboxylate (Abstr., 1909, i, 106), three complicated substances were obtained, two being isomerides of the formula $C_{22}H_{21}O_{13}N$, and the third having the composition $C_{22}H_{21}O_{12}N$. It is now shown that ethyl hexahydroxydiphenylaminetetracarboxylate, prepared by condensation of ethyl aminophloroglucinoldicarboxylate in cold alcoholic solution, is the parent substance of these compounds. Cold nitric acid converts it into a mixture in equal parts of the lactonic ester, $C_{22}H_{21}O_{13}N$, and the ester, $C_{22}H_{21}O_{12}N$ (*loc. cit.*, p. 107). The ester, $C_{24}H_{27}O_{14}N$, is consequently regarded as an intermediate stage in the action of nitric acid on ethyl phloroglucinol'dicarboxylate; alcohol is subsequently eliminated from it in one of two ways.

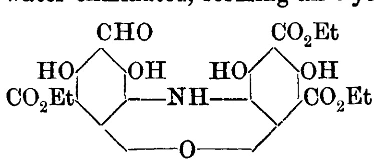


(I.)

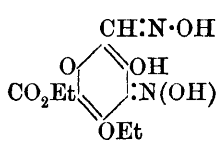


(II.)

Formula I represents the yellow ester, $C_{22}H_{21}O_{13}N$; formula II corresponds with the isomeric dark red ester, which contains the group >C:CO, characteristic of the ketens. This may be reduced by sulphurous acid or by boiling with alcohol, two atoms of hydrogen being added and water eliminated, forming an hydroxyaldehyde with a *p*-oxazine ring (annexed formula). Reduction with zinc dust and acetic acid converts this aldehyde into the corresponding alcohol.



By the action of hydroxylamine, the oxazine ring is broken, the nitrogen eliminated as ammonia, and the two products obtained have the formulæ:



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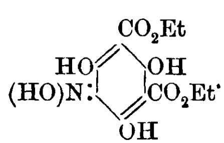


Diethyl tetrahydroxybenzenedicarboxylate, prepared by boiling the hydrochloride of ethylaminophloroglucinoldicarboxylate with water, forms long, colourless needles, m. p. 116—117°, and dissolves in sodium carbonate with a red, in ammonia with a reddish-yellow, coloration.

Ethyl hexahydroxydiphenylaminetetracarboxylate, $C_{24}H_{27}O_{14}N$, was obtained in colourless, glistening, obliquely-cut prisms or four-sided plates, m. p. 189—190° (corr.). The *acetyl* derivative crystallises from alcohol in heavy, four-sided plates, m. p. 211—212° (corr.). A by-

product of the condensation is a substance, $(C_{22}H_{21}O_{13}N)_x$, separating in intensely yellow-coloured needles, m. p. 265° (decomp.), which is regarded as a polymeride of the lactonic ester.

Reduction of the aldehyde ester, $C_{22}H_{21}O_{12}N$, converts it into the corresponding *alcohol*, $C_{22}H_{23}O_{12}N$, which crystallises in golden-yellow needles, m. p. 188—190° (corr.). Decomposition of this aldehyde with hydroxylamine yields an *oxime*, $C_{12}H_{14}O_7N_2$, crystallising in pointed, dark red prisms, m. p. 137—138°, together with an *oxime*, $C_{12}H_{13}O_8N$, which separates in yellow needles, m. p. 140—141°. The latter compound is also obtained by the action of hydroxylamine on ethyl tetrahydroxybenzenedicarboxylate.

The *hydrochloride* of *aminophloroglucinol*, $C_6H_2(OH)_3 \cdot NH_2$, prepared by reduction of nitrophloroglucinol with zinc and hydrochloric acid, was obtained in large, colourless plates (decomp. 230°). Condensation of this in alcoholic solution gave a dark violet substance insoluble in all reagents.

A weak solution of ammonia in methyl alcohol converts diethylphloroglucinoldicarboxylate into the corresponding methyl ether, which conversely is converted by ammonia in ethyl alcohol into the ethyl ester. The *dimethyl* ester forms colourless needles, m. p. 145—146°. The ethyl ester is not converted by prolonged boiling with methyl alcohol.

The *methyl* ester *amide* of phloroglucinoldicarboxylate separates in lancet shaped crystals, m. p. 240° (decomp.).

Similarly, diethyl malonate, when left in contact with methyl-alcoholic ammonia for some days at 10°, is converted into dimethyl malonate.

E. F. A.

Preparation of Halogen Anthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 217552).—When α- or β-chloroanthraquinone is treated with fuming sulphuric acid (40% anhydride) or with chlorosulphonic acid at 180°, a mixture of two sulphonic acids is obtained; these can be separated by fractional crystallisation, or by subsequent fusion with potassium hydroxide, yielding a mixture of anthrapurpurin and flavopurpurin. 1 : 8-Dichloroanthraquinone under similar conditions forms 1 : 8-dichloroanthraquinone sulphonic acid.

F. M. G. M.

[Preparation of Anthraquinone Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 220581).—A tabulated list of compounds prepared by the condensation of 4-amino-1-benzoylaminoanthraquinone with numerous halogenated aminoanthraquinones in boiling nitrobenzene solution in the presence of cupric chloride and sodium acetate. The colours of the solutions in concentrated sulphuric acid, pyridine, and when dyed on wool are described in the original.

F. M. G. M.

Preparation of Nitrogen Derivatives of Anthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 218571).—When aminoanthraquinones and epichlorohydrin are boiled together in acetic acid solution, condensation takes place, yielding compounds of value in the colour industry; the products thus obtained from α-amino-

anthraquinone, 1 : 5-diaminoanthraquinone, 1 : 4-aminohydroxyanthraquinone, and *p*-diaminoanthrarufindisulphonic acid are mentioned, and the colour of their solution in various solvents tabulated.

F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 220579).—The condensation of aminoanthraquinones with halogen ketones of the general formula H·R·CO·R·H, where R is a substituted or unsubstituted aromatic or aliphatic residue, and H a halogen, yields products of the type: A·NH·R·CO·R·NH·A; A = anthraquinone residue.

The patent contains particulars of the condensation of 1-aminoanthraquinone with 4 : 4′-dichlorobenzophenone and with α : 4-dichloroacetophenone in the presence of cuprous chloride and sodium acetate in boiling nitrobenzene solution. The colours of these substances in various strengths of sulphuric acid solution are tabulated.

F. M. G. M.

Retene. A. HEIDUSCHKA and E. SCHELLER (*Arch. Pharm.*, 1910, **248**, 89—101).—Tetrabromoretene can be obtained in good yield by adding bromine to retene, heating the mixture on the water-bath until the evolution of hydrogen bromide and bromine ceases, washing the mixture with boiling alcohol, and crystallising the residue from carbon disulphide. By treating its solution in boiling acetic acid with a hot mixture of chromic and acetic acids, *tribromoretenequinone*, $C_{18}H_{13}Br_3O_2$, m. p. 180°, is obtained, and also when the oxidation is effected by boiling acetic and fuming nitric acids. In its behaviour the quinone is quite analogous to retenequinone, yielding *tribromoresazine*,

$$C_{16}H_{13}Br_3{<}{\begin{smallmatrix}C:N\\C:N\end{smallmatrix}}{>}C_6H_4,$$

m. p. 255°, and *tolutribromoresazine*, $C_{16}H_{13}Br_3{<}{\begin{smallmatrix}C:N\\C:N\end{smallmatrix}}{>}C_7H_6$, m. p. 275—280°, in the usual way, reacting with ethereal hydrazines to form *tribromoretenequinonephenylhydrazone*, m. p. 245°, and the corresponding p-*nitrophenylhydrazone*, m. p. above 350° (decomp.), *diphenylhydrazone*, $C_{18}H_{13}OBr_3{:}N{\cdot}NPh_2$, m. p. 260—265°, *α-naphthylhydrazone*, m. p. above 300°, *β-naphthylhydrazone*, m. p. above 300° (decomp.), interacting with semicarbazide hydrochloride in boiling acetic acid to form the *semicarbazone*, $C_{16}H_{13}Br_3{<}{\begin{smallmatrix}C:N\cdot NH\cdot CO\cdot NH_2\\CO\end{smallmatrix}}$, m. p. 280—285°, and yielding with aminoguanidine hydrochloride, *tribromoretenequinoneaminoguanidine hydrochloride*, which decomposes at 218—220°, and yields by treatment with ammonium hydroxide the free *base*, $C_{16}H_{13}Br_3{<}{\begin{smallmatrix}CO\\C:N\cdot NH\cdot C(:NH)\cdot NH_2\end{smallmatrix}}$, m. p. 285° (decomp.). By nitration with fuming nitric acid at 0—5°, tribromoretenequinone yields *tribromonitroretenequinone*, $C_{18}H_{12}O_4NBr_3$, m. p. 255°. The following new retene derivatives are described: *toluresazine*, $C_{16}H_{16}{<}{\begin{smallmatrix}C:N\\C:N\end{smallmatrix}}{>}C_7H_6$, m. p. 155°; *retenequinonesemicarbazone*, m. p. 200°; *retenequinoneaminoguanidine*, and its *hydrochloride*, m. p. 253—254° (decomp.). The reaction between ethereal magnesium

phenyl bromide and an ethereal suspension of retenequinone leads to the formation of *dihydroxydiphenyldihydroretene*, $C_{30}H_{28}O_2$, m. p. 173—174°. C. S.

Influence of Constitution on the Rotatory Power of Optically Active Substances. III. Menthyl Esters of Terephthalic Acid, β-Naphthoic Acid, and Certain of their Reduction Products. Hans Rüpe [with F. Münter] (*Annalen*, 1910, **373**, 121—128. Compare Abstr., 1903, i, 565; 1909, i, 927). —A comparison of the optical rotatory powers of the menthyl esters of terephthalic acid, β-naphthoic acid, muconic acid (compare Hilditch, Trans., 1909, **95**, 1570), benzoic acid, α-naphthoic acid, and of the corresponding hydrogenated acids, the results of which may be summarised as follows:

(1) The menthyl esters of the acids with an ethylene linking in the Δ^2- or βγ-position have roughly the same rotatory power as the corresponding esters of the completely saturated acids.

(2) The reduced benzenoid derivatives are not so optically active as the corresponding benzenoid compounds; similarly, menthyl muconate is far more active than the menthyl ester of αβ-dihydromuconic acid, βγ-dihydromuconic acid, or adipic acid; menthyl $\Delta^{1:4}$-dihydroterephthalate is, however, slightly more active than menthyl terephthalate.

(3) In the muconic, benzoic, and α-naphthoic acid series, the acids with the ethylene linking in the αβ(Δ^1)-position are more active than the corresponding acids with the ethylene linking in the βγ(Δ^2)-position; on the other hand, the optical activities of the menthyl esters of Δ^2-tetrahydroterephthalic acid and Δ^3-dihydro-β-naphthoic acid are greater than those of the corresponding Δ^1-acids.

The following esters are prepared by the action of the acid chloride on menthol in the presence of pyridine; the [α] values refer to 10% chloroform solutions unless otherwise stated: *dimenthyl terephthalate*, $C_{28}H_{42}O_4$, white needles, m. p. 75°, $[\alpha]_D^{20}$ $-102{\cdot}64°$; *dimenthyl* $\Delta^{1:4}$-*dihydroterephthalate*, $C_{28}H_{44}O_4$, white needles, m. p. 68°, $[\alpha]_D^{20}$ $-104{\cdot}55°$; *dimenthyl* Δ^1-*tetrahydroterephthalate*, $C_{28}H_{46}O_4$, white needles, m. p. 125°, $[\alpha]_D^{20}$ $-69{\cdot}42°$; *dimenthyl* trans-Δ^2-*tetrahydroterephthalate*, $C_{28}H_{46}O_4$, small, white needles, m. p. 64°, $[\alpha]_D^{20}$ $-76{\cdot}09°$; *dimenthyl* trans-*hexahydroterephthalate*, $C_{28}H_{48}O_4$, slender, white needles, m. p. 132—133°, $[\alpha]_D^{20}$ $-74{\cdot}72°$; *menthyl β-naphthoate*, $C_{21}H_{26}O_2$, long, colourless prisms, m. p. 75—76°, $[\alpha]_D^{20}$ $-91{\cdot}30°$ (in benzene); *menthyl* Δ^2-*dihydro-β-naphthoate*, $C_{21}H_{28}O_2$, colourless, viscid oil, b. p. 218°/10·5 mm., $[\alpha]_D^{20}$ $-41{\cdot}40°$ (in benzene); *menthyl* Δ^3-*dihydro-β-naphthoate*, an oil which decomposes when heated, $[\alpha]_D^{20}$ $-53{\cdot}14°$ (in benzene); *menthyl tetrahydro-β-naphthoate*, $C_{21}H_{30}O_2$, colourless, viscid oil, b. p. 218°/11 mm., $[\alpha]_D^{20}$ $-53{\cdot}04°$ (in benzene). W. H. G.

Artificial Camphor. Eugène Darmois (*Compt. rend.*, 1910, **150**, 925—927).—Although commercial artificial camphor shows only feeble optical rotatory power, it is possible to obtain a strongly active, synthetic product by working at low temperatures. Algerian

turpentine (containing α-pinene, $[\alpha]_D$ 50·5°) has been converted into borneol hydrobromide; the magnesium derivative of this yielded a mixture of *d*-borneol and *l*-*iso*borneol, which, on oxidation with chromic acid in the cold, gave *d*-camphor, identical with the natural product, but contaminated with 7% of *l*-camphor. Under the same conditions, a French turpentine containing 96% of *l*-pinene and 4% of *d*-pinene gave a mixture of *l*-camphor with 10% of *d*-camphor (compare Hesse, Abstr., 1906, i, 376). W. O. W.

Thiocamphorimide. GIUSEPPE ODDO and ANNA MANNESSIER (*Gazzetta*, 1910, **40**, i, 43—51).—*Thiocamphorimide*, $C_8H_{14}{<}^{CS}_{CS}{>}NH$, prepared by the action of phosphorus pentasulphide on camphorimide, forms golden-yellow scales or prisms, m. p. 135°, $[\alpha]_D$ +63·29°, which smell faintly of garlic and are tasteless; it has acid properties, and with alkali hydroxides it gives orange-yellow solutions, from which it can be reprecipitated unchanged; it dissolves in cold concentrated sulphuric acid, giving an intense red coloration, but determinations of the molecular weight in sulphuric acid by Oddo and Scandola's method (Abstr., 1908, ii, 353) gave half the theoretical value, so that the nitrogen assumes a basic function, the acid sulphate,

$$C_8H_{14}{:}[CS]_2{:}NH_2{\cdot}HSO_4,$$

being formed. A solution of thiocamphorimide in aqueous-alcoholic potassium hydroxide solution gives precipitates with salts of the following metals: zinc; *lead*, $Pb(C_{10}H_{14}NS_2)_2$; barium; *silver*, $C_{10}H_{14}NS_2Ag$; and mercury(ic). *Benzoylthiocamphorimide*,

$$C_{10}H_{14}NS_2Bz,$$

forms intensely yellow, rhombic crystals, m. p. 156—157°. When thiocamphorimide is boiled with aqueous alkali solution until the evolution of hydrogen sulphide ceases, camphoric acid is obtained as the sole product. When heated in a sealed tube with concentrated ammonium sulphide solution, thiocamphorimide is converted into camphorimide, whilst with sodium hydrogen sulphide, camphoric acid alone is obtained. Oxidation of thiocamphorimide by means of alkaline permanganate yields camphorimide. T. H. P.

Preparation of Terpene Alcohols from Pinene Hydrochloride. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 219243). The *alcohol*, $C_{10}H_{17}{\cdot}OH$, is prepared by heating pinene hydrochloride at about 140—160° in the presence of water with freshly prepared mildly basic reagents, such as calcium hydroxide, the oxides or hydroxides of zinc or lead, or the alkali or alkaline earth carbonates, and subsequent extraction and distillation of the product; the new alcohol sublimes at 149—150°, has b. p. 204—206°/760 mm. or 90—100°/20 mm., and is of therapeutic value; when heated with dilute mineral acids, water is eliminated, with the formation of camphene. F. M. G. M

Spanish Oil of Turpentine. OBDULIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1909, **7**, 442—448).—Turpentine oil, distilled in a current of steam, from the resin of *Pinus Halepensis*, grown in Andalusia, has

$D^{20} = 0.859$; $[\alpha]_D$ $-8.73°$, and n_D 1·4654. It is thus very different in physical properties from French oil of turpentine. When treated in the usual way with hydrogen chloride, it gives 35—40% of a solid monohydrochloride and 60—65% of a liquid monohydrochloride. The hydrochloride when subjected to Grignard's reaction is converted into a *borneol*, m. p. 115—116°, $[\alpha]_D$ $-10°$ in 5% alcoholic solution, which is not identical with ordinary borneol. The yield is 90% of the theoretical, 10% of a *dihydrodicamphene*, $C_{20}H_{34}$, being also formed. When oxidised with potassium dichromate and sulphuric acid, the borneol gives a camphor, the properties of which are being studied.

The *nitrosochloride* of the pinene, m. p. 95°, does not combine readily with ammonia; a *nitrolamine* was, however, obtained with difficulty, but could not be crystallised. The *salicylidene* and *furfurylidene* derivatives of the latter are not identical with the compounds described by Leach (Trans., 1907, **91**, 1). W. A. D.

Hydrogenation of Turpentine Oil. G. VAVON (*Compt. rend.*, 1910, **150**, 1127—1130. Compare this vol., i, 52).—In view of the fact that the α-pinene employed in previous experiments was not a homogeneous substance, the author has repeated them, employing different fractions of commercial turpentine. All the fractions, whether from French, German, or American oils, gave on reduction hydrocarbons having very variable rotatory powers ($[\alpha]_D$ $+23.8°$ to $-23.8°$), but otherwise having the same physical constants as the liquid obtained from α-pinene. The values for the specific rotations were plotted in the form of curves, and the composition of the products deduced from Biot's law of mixtures. In general, the results are in agreement with those previously obtained, and confirm the conclusions of Darmois (this vol., i, 52) on the composition of turpentine oil. W. O. W.

Liquid Pinene Hydrochloride. PHILIPPE BARBIER and VICTOR GRIGNARD (*Bull. Soc. chim.*, 1910, [iv], 7, 342—350).—In a previous paper (Abstr., 1909, i, 501) the authors applied the method of hydration to the study of the hydrocarbons which accompany natural pinene. In the present communication they have with the same object in view examined the liquid hydrochloride formed to a small extent, along with the solid hydrochloride, when pinene is treated with hydrogen chloride. The results indicate that nopinene may be present in natural pinene to the extent of about 5%.

The liquid hydrochloride, b. p. 79—81°/13 mm., was treated with magnesium turnings in presence of some ethyl bromide, and the magnesium compounds formed oxidised by a current of dry oxygen. On fractionation a neutral portion, b. p. 155—170°, an alcohol fraction, b. p. 170—220°, and a viscous product, $(C_{10}H_{17})_2$, b. p. 183°/14 mm., were obtained. The second fraction alone was examined. It consisted of a mixture of alcohols and hydrocarbons, which were separated by Tschugaeff's process. From the purified alcohols some borneol, derived from solid hydrochloride, present as an impurity in the parent material, was isolated. The residual liquid was not homogeneous, since it furnished a mixture of phenylurethanes, of which extreme fractions had m. p. 91° and 115° (approx.). It was therefore

oxidised with nitric acid, and yielded a liquid ketone consisting apparently mainly of fenchone. It was treated with hydroxylamine, and gave (1) camphoroxime, (2) *l*-fenchoneoxime, and (3) an oxime, m. p. 161—162°, somewhat resembling camphoroxime [monoclinic: $a:b:c = 0{\cdot}95:1:0{\cdot}7218$, $\beta = 100°39'$ (Zander)]. The last product is the principal substance formed, and for the identification of the ketone yielding it, the mixed ketones were treated by sodamide (Semmler, Abstr., 1906, i, 681) and the resulting amides separated into *l*-dihydrofencholamide, m. p. 94°, *r*-dihydrofencholamide, m. p. 115°, and a third *amide*, m. p. 108°, $\alpha_D = -0°35'$, crystallising in brilliant spangles, and which yielded on hydrolysis an *acid*, b. p. 143°/11 mm. and $\alpha_D - 1°24'$ in a 15 cm. tube. At present it is impossible to say whether these derivatives are due to a new ketone or to an optically active racemic form of fenchone.

The results indicate that the liquid pinene hydrochloride contains bornyl chloride, fenchyl chloride, and probably tertiary chlorides, the second of these being propably derived from nopinene.

T. A. H.

Essential Oils. HEINRICH HAENSEL (*Bericht von Heinrich Haensel*, October—March, 1909—1910. Compare Abstr., 1909, i, 815).—The leaves of *Sambucus ebulus* (Herba ebuli) yielded 0·0763% oil, of dark brown colour and unpleasant spicy odour; it had D^{15} 0·8998, acid number 250·9, and ester number 46·0. After saponification the oil developed an odour recalling that of apricots or peaches, probably due to the presence of an alcohol. No phenol was present.

The root of *Ononis spinosa* gave 0·02% of oil, composed of a liquid portion, D^{15} 0·9917, and a solid portion.

"Distilled lime oil" gave the following results: D^{15} 0·8612, acid number 1·8, ester number (one hour) 12·5, and acetyl ester number (0·75 hour) 53·42; limonene was detected as well as *l*-terpineol (compare Burgess and Page, Trans., 1904, **85**, 414) and bisabolene.

Vitex agnus castus seeds furnished 0·47% of oil, D^{15} 0·8960, acid number 7·41, ester number 24·0, acetyl ester number 40·0, having a pungent, spicy odour. It contained a phenol with an empyreumatic odour. On saponification, the odour of the oil became pepper-like, and after acetylation, it lost entirely its unpleasant odour.

Syrian peppermint oil had D^{15} 0·9130, acid number 0·0, ester number (one hour) 22·25, acetyl ester number (one hour) 151·5.

Ylang-ylang oil, prepared by extraction of the flowers with light petroleum, had D_4^{30} 0·940, n_D^{30} 1·4920, ester number 135, acetyl ester number 208.

T. A. H.

Oil of Samphire. MARCEL DELÉPINE (*Compt. rend.*, 1910, **150**, 1061—1063.* Compare Abstr., 1909, i, 642; Borde, *ibid.*, i, 945).—Fractionation of over a kilogram of samphire oil has enabled the author to identify limonene, cymene, the methyl ether of thymol, and a *d*-pinene having $[\alpha]_D + 47°45'$, in addition to the substances already recognised.

W. O. W.

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 468—473.

Examination of the Solid Constituent of Turpentine from Pinus silvestris, of its Derivatives, and of French Colophony. STANISLAUS LESKIEWICZ (*J. pr. Chem.*, 1910, [ii], 403—420).—Schkateloff has suggested that all the acids, such as abietic acid, pimaric acid, and sylvic acid, obtained from the common resins and turpentines, are identical with, or are simple transformation products of, his α-sylvic acid (*Mon. Sci.*, **22**, 217; [ii], **22**, 548). This suggestion receives support from the author, who gives the name sapic acid to all the preceding acids. The acid, obtained from different sources, does not form crystalline salts, and its rotatory power is very easily changed by heat. Thus the sapic acid, $C_{20}H_{30}O_2$, obtained by the repeated crystallisation of the resin acids from the turpentine of *Pinus silvestris* from anhydrous acetone, and finally from alcohol and water below 60°, has m. p. 142—144° and $[\alpha]_D^{19}$ $-105{\cdot}3°$ in alcohol ($c=9{\cdot}9296$). The sapic acid, prepared from the colophony of turpentine, has m. p. 145—147° and $[\alpha]_D^{18}$ $-35{\cdot}16°$ ($c=10{\cdot}002$), whilst the sapic acid from the colophony of *Pinus maritima* has m. p. 146—148° and $[\alpha]_D^{19}$ $14{\cdot}21°$ ($c=10{\cdot}0278$). These acids are easily converted into the sylvic acids, of which *l*-sylvic acid (Schkateloff's β-sylvic acid) has been obtained pure in the following manner. The sapic acid or the crude colophony of *Pinus silvestris* is dissolved in glacial acetic acid, and the hot solution is treated with a few drops of concentrated hydrochloric acid; the crude *l*-sylvic acid, which separates from the cold solution, is purified by means of the crystalline sodium salt. Pure *l*-sylvic acid, $C_{20}H_{30}O_2$, has m. p. 171—172°, $[\alpha]_D^{15}$ $-102{\cdot}85°$ in alcohol ($c=10$), and forms crystalline potassium and ammonium salts. *l*-Colophonic acid, $C_{20}H_{30}O_2$, obtained by rapidly distilling the sapic acids, the colophony of *Pinus silvestris* or of *Pinus maritima*, or *l*-sylvic acid, has m. p. 191—192° and $[\alpha]_D^{15}$ $-56{\cdot}13°$ ($c=5{\cdot}0096$); probably it is identical with Klason and Köhler's α-colophonic acid.

C. S.

Composition of Natural Scammony. A. GORIS and G. FLUTEAUX (*Bull. Sci. pharm.*, 1910, Jan., Reprint, 2 pp.).—A specimen of this gum-resin collected by Guigues was found to have the following percentage composition: moisture, 5; ash, 7·18; matter soluble in alcohol (95), 79·82; matter insoluble in alcohol (by difference), 8. 66·7% of the gum-resin was soluble in ether. The specific rotation of the resin soluble in alcohol was α_D $-21{\cdot}47°$, and of that soluble in ether $-24{\cdot}26°$ (compare Guigues, Abstr., 1908, ii, 995). The rather high percentage of ash was due to contamination of the scammony by sand carried by the wind. The ash contained ferric oxide, alumina, silica, and lime. No starch was found in the product.

T. A. H.

Resolution of Racemic Cyanohydrins by Emulsin. KARL FEIST (*Arch. Pharm.*, 1910, **248**, 101—104).—The author is unable to confirm Auld's statement that an active benzaldehydecyanohydrin is produced directly from benzaldehyde, potassium cyanide, and hydrochloric acid (Trans., 1909, **95**, 929).

The production of *l*-benzaldehydecyanohydrin by the action of

emulsin on the *dl*-form (Abstr., 1909, i, 589) has induced the author to examine in a similar manner other cyanohydrins, active forms of which are produced by synthesis in the presence of emulsin (Rosenthaler, Abstr., 1909, i, 622). Success is attained only under suitable conditions of concentration.

dl-Acetaldehydecyanohydrin, 1·8 grams, is added to 5 grams of emulsin in 20 grams of water, and air is passed through the mixture for twenty-four hours; the ethereal extract is evaporated; the solution of the residue in chloroform is distinctly lævorotatory. The solution obtained in a somewhat similar manner from 4 grams of *dl*-cinnamaldehydecyanohydrin is also lævorotatory, but the conditions could not be obtained for the resolution of *dl*-*iso*butaldehydecyanohydrin. The rotations of the cyanohydrins thus obtained are in the opposite directions to those of the cyanohydrins produced by synthesis in the presence of emulsin. C. S.

Hydrolysis of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, **248**, 105—112. Compare Abstr., 1909, i, 74).—The first step in the hydrolysis of amygdalin by emulsin is the formation of dextrose and mandelonitrileglucoside (compare Auld, Trans., 1908, **93**, 1276). The latter may then undergo fission either into equal molecular quantities of benzaldehyde, hydrogen cyanide, and dextrose, or into dextrose and benzaldehydecyanohydrin, which then undergoes secondary decomposition. Feist's contention that the latter is the case because *d*-benzaldehydecyanohydrin is obtained (Abstr., 1908, i, 437) is baseless, since benzaldehyde and hydrogen cyanide yield the *d*-cyanohydrin in the presence of emulsin (Abstr., 1908, i, 817). His attempt to support his position by parallel experiments in which emulsin acts on amygdalin and on benzaldehyde, hydrogen cyanide, and dextrose (this vol., i, 123) is equally unfortunate, since the author shows that the results are largely influenced or even reversed by the quality of the emulsin employed.

The author inclines to the view that *d*-benzaldehydecyanohydrin is partly a primary and partly a secondary product of the hydrolysis of amygdalin by emulsin. He shows that hydrogen cyanide is produced within two minutes of the commencement of the hydrolysis, and that therefore all the materials, benzaldehyde, hydrogen cyanide, and emulsin, requisite for the synthetic production of the *d*-cyanohydrin are present in the system. An argument in favour of the primary formation of the *d*-cyanohydrin is the fact that it is still present in the products of hydrolysis even when the hydrogen cyanide has been destroyed by the addition of nickel formate. C. S.

Principles of Atractylis gummifera (Sicilian Masticogna). FRANCESCO ANGELICO (*Gazzetta*, 1910, **40**, i, 403—411. Compare Abstr., 1907, ii, 122, 801).—The valeric acid obtained by the hydrolysis of the poisonous principle of *Atractylis gummifera* is the normal acid, and the carbohydrate also obtained is a hexose, which, with phenylhydrazine, yields phenylglucosazone.

The principle may be detected by the two following reactions: (1) If a crystal of the substance is treated with concentrated sulphuric

acid to which a few drops of formaldehyde solution and then water have been added, it assumes a yellow colour, addition of water then resulting in the formation of a blue coloration at the surface of contact of the two liquids. Further addition of water gives a clear blue liquid, the colour of which persists for some days. The coloration disappears if the liquid is rendered alkaline, but reappears on acidification. This reaction may also be employed for revealing the presence of formaldehyde, and is capable of detecting the aldehyde in a liquid containing 3 drops of the 40% solution per litre. The reaction is not given by other aliphatic aldehydes, but with dextrose a red coloration is obtained. (2) An aqueous solution of an aromatic aldehyde containing a hydroxy- or alkyloxy-group, when added to a sulphuric acid solution of the poisonous principle, gives a coloration which varies with the concentration from magenta-red to cochineal-red, or red with a slight violet tinge. This coloration, which is given by piperonaldehyde, vanillin, opianic acid, or *p* hydroxybenzaldehyde, is not destroyed by diluting the solution with water, but disappears on addition of alkali, subsequent acidification restoring it. The same coloration is given by furfuraldehyde, cinnamaldehyde, and salicylaldehyde, but with the last two compounds the colour disappears on adding water. In dilute solution, the coloration only causes a weakening of the whole spectrum, but with more concentrated solutions, an absorption band in the green having the mean wavelength 5270 is observed. T. H. P.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1910, 40, i, 391—403). —The author has succeeded in oxidising picrotin so as to obtain *a*-picrotinic acid alone, instead of the mixture of isomeric acids, $C_{15}H_{18}O_8$, formed when the oxidation is effected by means of alkaline permanganate solution (compare Abstr., 1909, i, 318).

a-Picrotinic acid is a monobasic acid, and forms white crystals, m. p. 245° (decomp.). It is stable towards alkaline permanganate, does not react with hydroxylamine, phenylhydrazine, or ethyl iodide, but gives a complex mixture when treated with chromic acid mixture, and with acetic anhydride yields a syrupy product. Its *calcium* salt and *ethyl* ester, m. p. 194°, were prepared. When heated at its m. p., the acid yields a small proportion of a *substance*, forming white crystals, m. p. 230° (decomp.).

Reduction of *a*-picrotinic acid by means of hydriodic acid and red phosphorus results in the formation of the monocarboxylic acid, $C_{15}H_{18}O_4$, obtained by Oglialoro and Forte (Abstr., 1892, 349) by the reduction of picrotin; the *silver* salt of this acid was prepared. Oxidation of the acid, $C_{15}H_{18}O_4$, by means of permanganate in alkaline solution yields, according to the proportion of oxidising agent employed, one of the three following dicarboxylic acids: (1) an optically inactive *acid*, $C_{13}H_{14}O_2(CO_2H)_2,\frac{1}{2}H_2O$, which crystallises in shining, white needles, m. p. 188°, has the normal molecular weight in freezing acetic acid, and does not contain a carbonyl group; (2) an *acid*, $C_{13}H_{12}O_6$, which forms white, rhombohedral plates, m. p. about 110°, decomp. at about 125—130°; the *silver* salt was prepared; (3)

the *acid*, $C_{13}H_{12}O_7$, m. p. 175°, which is probably a derivative of malonic acid, and the salts of which, on gentle heating, yield a small proportion of a *substance*, m. p. about 260°; the *silver* salt was prepared.

When α-picrotinic acid is subjected to prolonged boiling with 25% sulphuric acid, it is converted into a pale yellow, oily *ketone*, $C_{14}H_{16}O_4$, which yields an *oxime*, m. p. 208—209° (decomp.), and a *semicarbazone*, m. p. 226° (decomp.), and, on oxidation with acid permanganate solution in the cold, gives a monocarboxylic *acid*, $C_{14}H_{16}O_4$, forming white, silky needles, m. p. 165°, and having the normal molecular weight in freezing acetic acid. Oxidation of this acid by alkaline permanganate solution on a water-bath gives the acid, $C_{13}H_{12}O_6$, m. p. 110°, formed by the oxidation of the acid, $C_{15}H_{18}O_4$ (*vide supra*).

From these results the conclusion is drawn that α-picrotinic acid is represented by the formula $CO_2H\cdot C_{14}H_{14}O_2(OH)_3\colon O$. T. H. P.

Action of Light on Dyes. KURT GEBHARD (*Zeitsch. angew. Chem.*, 1910, **23**, 820—827).—The author has confirmed the theory (*Zeitsch. angew. Chem.*, 1910, **22**, 2484) that the bleaching of dye solutions or of dyed tissues by light is due to the primary formation of a peroxide of the dye. The peroxide is best detected by acidified potassium iodide and starch, by alkaline potassium permanganate, or by diphenylamine and concentrated sulphuric acid; chromic, molybdic, and titanic acids do not indicate the presence of a peroxide, this fact furnishing one of the author's several arguments against the theory of the primary formation of hydrogen peroxide.

The rays which are most effective in the production of the peroxide are those complementary to the colour of the dye. Blue, violet, and ultraviolet rays exert a decomposing action on the peroxide, or occasion a transference of the active oxygen to unattacked molecules of the dye.

The author utilises Mumm's theory of oxidation in the presence of water (Abstr., 1907, ii, 527), and shows by an electrolytic experiment that the perhydroxyl ions are instrumental in bleaching the dye. C. S.

Advances in Vat Dyes. RENE BOHN (*Ber.*, 1910, **43**, 987—1007).—A survey of recent advances in the field of the vat dyes. A lecture delivered before the German Chemical Society. J. J. S.

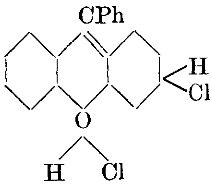
Condensation of α- and β-Naphthols with Ethyl Acetoacetate. A. BACOVESCU (*Ber.*, 1910, **43**, 1280—1282. Compare Bartsch, Abstr., 1903, i, 648).—The condensation of β-naphthol and ethyl acetoacetate has been carried out in the presence of concentrated sulphuric acid and anhydrous ether. A 30% yield of a β-methylnaphthacoumarin, $C_{10}H_6\begin{cases}O\text{——}CO\\ CMe\colon CH\end{cases}$, is obtained when the sulphuric acid is added gradually to the ice-cold mixture and then the whole kept at the ordinary temperature for twenty days. It crystallises in

colourless needles, m. p. 182—183°, and its solutions in alcohol or concentrated sulphuric acid have a blue fluorescence. It yields a *dibromide*, but this loses hydrogen bromide readily, yielding the *bromo*-derivative, $C_{10}H_6<\begin{matrix}O\text{——}CO\\ CMe{:}CBr\end{matrix}$, m. p. 148°. The *nitro*-derivative has m. p. 258°.

When α-naphthol is used, a 60% yield of Bartsch's 4-methyl-2-naphthacoumarin is formed, and the same product can be obtained when hydrogen chloride is used as the condensing agent. J. J. S.

Xanthen and Triphenylmethane. FRIEDRICH KEHRMANN (*Annalen*, 1910, **372**, 287—355).—A further contribution to the chemistry of xanthen derivatives, being, in the main, an extension of the investigations of the author and Dengler (compare Abstr., 1908, i, 1002; Abstr., 1909, i, 249). The salts of quinolphthalein ethers (compare Green and King, Abstr., 1907, i, 933), unlike those of fluorescein trimethyl ether (compare Kehrmann and Dengler, Abstr., 1909, i, 249), are found to be hydrolysed by water with great rapidity, an observation which led to a study of the phthaleins and benzeins.

The author criticises adversely the views of von Baeyer (compare Abstr., 1905, i, 281), and replies to the objections raised by Kropp and Decker (compare Abstr., 1909, i, 248); further, it is considered probable that the intensely coloured hydrochloride of phenylxanthenol (compare Gomberg and Cone, this vol., i, 55) has the formula (I), and when heated passes, with elimination of hydrogen chloride, either into the colourless carbinol chloride (II) or into the coloured oxonium chloride (III).



(I.)

$$O<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CPhCl$$

(II.)

$$Cl\cdot O<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CPh$$

(III.)

The view advanced by Gomberg and Cone (*loc. cit.*), that the salts of the phenylacridols are quinocarbonium salts, is held to be quite untenable.

Fluorescein and resorcinolbenzein are regarded by von Liebig as quadrimolecular complexes (*Naturforscherversammlung*, Salzburg; compare also Abstr., 1909, i, 98). Mol.-wt. determinations by the cryoscopic method, using phenol as the solvent, show that these substances, likewise 3-hydroxymethylfluorone, are undoubtedly unimolecular.

[With OTTO DENGLER.]—3 : 6-Diacetylamino-9-phenylxanthonium chloride (diacetylphenorosamine chloride) crystallises in flat, reddish-brown needles (compare Abstr., 1908, i, 1002); the *chromate*, orange-red needles; *platinichloride*, brick-red, crystalline powder, and *iodide*, orange-yellow needles, were analysed. The chloride, when treated with dilute aqueous sodium hydroxide, yields a bluish-red *substance*, which is converted by hot water into the carbinol *base*, $C_{25}H_{24}O_4N_2$, crystallising in colourless needles, m. p. 248° (decomp.).

Phenorosamine chloride (3 : 6-*diamino*-9-*phenylxanthonium chloride*),

$CPh{<}{\begin{smallmatrix}C_6H_3(NH_2)\\C_6H_3(NH_2)\end{smallmatrix}}{>}OCl$, obtained by boiling the diacetyl derivative with hydrochloric acid, crystallises in slender, red needles with a blue reflex, and dissolves in alcohol and water, forming intensely fluorescent solutions; it dyes silk pink with a yellow fluorescence; the *platinichloride* is a vermilion powder.

3-*Amino*-6-*hydroxy*-9-*phenylxanthonium chloride*, $C_{19}H_{14}O_2NCl$, crystallises in brick-red leaflets with a blue reflex; the *platinichloride* is a scarlet, crystalline powder.

Acetylaminophenylfluorone (*loc. cit.*), when acted on by methyl sulphate in hot nitrobenzene, yields 3-*acetylamino*-6-*methoxy*-9-*phenylxanthonium methyl sulphate*, $CPh{<}{\begin{smallmatrix}C_6H_3(NHAc)\\C_6H_3(OMe)—\end{smallmatrix}}{>}O{\cdot}SO_4Me$, crystallising in brick-red needles with a blue reflex; the *aurichloride*, *chromate*, *iodide*, and *platinichloride* are crystalline, orange-yellow powders; the chloride, when hydrolysed by boiling dilute hydrochloric acid, yields 3-*amino*-6-*methoxy*-9-*phenylxanthonium chloride*, crystallising in long, dark red needles with a green reflex; the *platinichloride*,

$$(C_{20}H_{16}O_2N)_2PtCl_6,$$

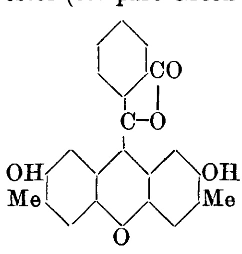
is brick-red.

[With KARL SCHEUNERT.]—The chloride of methyl 3 : 6-dimethoxy-9-phenylxanthonium-2′-carboxylate (compare Abstr., 1909, i, 249) is prepared most readily by the action of hydrogen chloride and methyl alcohol on 3 : 6-dimethoxyfluoran; it crystallises in lemon-yellow leaflets with a blue shimmer, and behaves, according to electrical conductivity measurements, as the chloride of a strong base; the *dichromate*, $(C_{23}H_{19}O_5)_2Cr_2O_7$, long, glistening, orange-red needles, m. p. 138°; *iodide*, red needles; *nitrate*, glistening, yellow leaflets, and *platinichloride*, crystalline, pale orange granules, were prepared.

The *chloride* of the corresponding *ethyl* ester, prepared in a similar manner, forms yellow leaflets with a blue reflex; the violet *iodide*, reddish-orange *bromide*, red *dichromate*, m. p. about 140°, and orange *platinichloride*, $(C_{24}H_{21}O_5)_2PtCl_6$, were prepared.

The *chloride* of *ethyl* 3:6-*diethoxy*-9-*phenylxanthonium*-2′-*carboxylate*, similarly prepared from 3 : 6-diethoxyfluoran, forms yellow leaflets with a blue reflex; the *platinichloride*, $(C_{26}H_{25}O_5)_2PtCl_6$, is a crystalline, yellow powder, m. p. 192°; the *bromide* is golden-yellow; the *iodide* is orange-red.

[With ROBERT SILZER.]—The *methosulphate* of quinolphthalein methyl ester (compare Green and King, Abstr., 1908, i, 1003) is converted by sodium nitrate into the corresponding *nitrate*, which forms yellowish-red crystals, the *platinichloride*, $(C_{23}H_{19}O_5)_2PtCl_6$, is garnet-red.



Toluquinolphthalein (annexed formula) is prepared by heating toluquinol with phthalic anhydride in the presence of stannic chloride; it crystallises in colourless needles, m. p. 298—300°; the *chloride*, $C_{22}H_{17}O_5Cl$, forms red needles, and is converted by hydrogen chloride and methyl alcohol into the *chloride* of the *methyl*

ester, which crystallises in brownish-red needles; the corresponding *platinichloride*, $(C_{23}H_{19}O_5)_2PtCl_6$, forms garnet-red granules.

Dimethyltoluquinolphthalein, prepared by the action of methyl iodide on an alkaline solution of the toluquinolphthalein, forms colourless crystals, m. p. 270° (decomp.); the *salts* are strongly hydrolysed in aqueous solutions; the *chloride* of the corresponding *methyl* ester, $C_{25}H_{23}O_5Cl$, obtained by treating the dimethyl ether with methyl alcohol and hydrogen chloride, crystallises in glistening, orange-red needles, and is hydrolysed very slowly in aqueous solutions; the *platinichloride*, $(C_{25}H_{23}O_5)_2PtCl_6$, is a crystalline, red powder; the *dichromate* forms small, garnet-red needles.

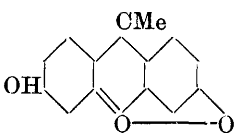
Quinolbenzein chloride, $CPh<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>OCl$ (compare von Baeyer, this vol., i, 252), is readily prepared by acting on a solution of quinol and benzaldehyde in glacial acetic acid with concentrated sulphuric acid and oxidising the xanthen derivative thus obtained by means of ferric chloride; the *nitrate*, $C_{19}H_{13}O_3{\cdot}NO_3$, forms small, glistening, dark red needles; the *dimethyl ether*, $OH{\cdot}CPh<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{matrix}>O$, obtained by treating an alkaline solution of quinolbenzein with methyl iodide, forms colourless crystals, m. p. 143°; the *salts* are hydrolysed to a great degree in aqueous solutions; the *platinichloride*,

$$(C_{21}H_{12}O_3)_2PtCl_6,$$

crystallises in dark red leaflets.

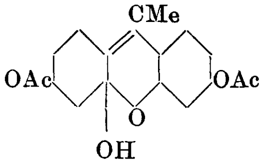
Toluquinolbenzein (2 : 7-*dihydroxy*-3 : 6-*dimethyl*-9-*phenylxanthen*-9-*ol*), prepared from toluquinol and benzaldehyde, forms a *chloride*, $C_{21}H_{17}O_3Cl$, crystallising in glistening, brownish-red needles; an aqueous solution of the salt, when treated with sodium hydrogen carbonate, yields a microscopic, crystalline, black *substance*, which is probably a quinhydrone of 1 mol. of the carbinol with 1 mol. of the quinonoid anhydro-base; the *chloride* of the *dimethyl ether* forms glistening, red needles, and is not hydrolysed in aqueous solutions; the *platinichloride*, $(C_{23}H_{21}O_3)_2PtCl_6$, is a crystalline, garnet-red powder.

[With S. M. Jones.]—The *stannichloride* of 3-hydroxymethylfluorone, $(C_{14}H_{11}O_3Cl)_2,SnCl_4$, prepared by heating resorcinol and 2 : 4-dihydroxyacetophenone with stannic chloride at 160—180°, forms large, dark red, glistening granules with a blue metallic reflex, and when treated with an aqueous solution of sodium acetate yields



3-*hydroxymethylfluroone* (annexed formula), crystallising in large, dark red plates with a blue reflex; the latter substance sinters at 229°, m. p. 238° (decomp.), and forms yellow solutions with an intense green fluorescence; the *chloride*, $C_{14}H_{11}O_3Cl$, forms reddish-yellow needles with a blue reflex; the *platinichloride*, long, lemon-yellow needles; *iodide*, orange-red leaflets; *bromide*, small, orange-red crystals, and *picrate*, lemon-yellow powder, were prepared; the *silver* salt is a brick-red powder. The compound described by Nencki and Sieber as acetylfluorescein (compare Abstr., 1881, 811) is identical with 3-hydroxymethylfluorone. The latter substance, when heated with

acetic anhydride and sodium acetate, yields 3 : 6-diacetoxyxanthone, m. p. 204° (compare Meyer and Conzetti, Abstr., 1897, i, 380), and the *acetyl* derivative of the corresponding xanthonecarbinol (annexed formula), which crystallises in yellow prisms, m. p. 200°. 3-Hydroxymethylfluorone is converted by glacial acetic acid and sodium nitrite into an *oximino*-



derivative, $O<\substack{O:C_6H_3(OH)\\ C_6H_3}>C\cdot CH:N\cdot OH$, which crystallises in stout, dark red prisms with a green, metallic reflex, m. p. 200° (decomp.), and is decomposed quantitatively by aqueous sodium hydroxide into 3 : 6-dihydroxyxanthone and hydrogen cyanide. The reduction of 3 : 6-dihydroxyxanthone with sodium amalgam leads to the formation of 3-*hydroxyfluorone*, $O<\substack{O:C_6H_3(OH)\\ C_6H_3}>CH$, a brick-red, crystalline powder with a blue reflex, which commences to darken at 275°, but does not melt at 320°; the solutions exhibit an intense, green fluorescence; the *chloride* forms yellow needles.

[With Xavier Vogt.]—Resorufin methyl ether (compare Nietzki, Dietze, and Mäckler, Abstr., 1890, 156), when acted on by methyl sulphate in nitrobenzene at 100°, yields 3 : 6-*dimethoxyphenazoxonium methosulphate*; the *chloride*, $N<\substack{C_6H_3(OMe)\\ C_6H_3(OMe)}>OCl$, and *platinichloride*, iridescent, bluish-green leaflets, m. p. 110—115°, were prepared.

3 : 6-*Dimethoxyphenazonium* salts, $N<\substack{C_6H_3(OMe)\\ C_6H_3(OMe)}>NPh\cdot X$, are prepared in the same manner from safranol methyl ether; the *chloride*, small, golden-yellow needles; *bromide*, orange-red leaflets with a blue reflex; *platinichloride*, orange leaflets; *dichromate*, yellowish-brown leaflets; *nitrate*, golden-yellow needles, and *iodide*, orange-red needles, were prepared; an aqueous solution of the bromide, when acted on by silver hydroxide, yields a distinctly alkaline solution of the azonium base, which absorbs carbon dioxide, forming the *carbonate*, obtained in yellow needles by evaporating the solution over concentrated sulphuric acid. W. H. G.

Thio-γ-pyrone Derivatives. Hermann Apitzsch and C. Kelber (*Ber.*, 1910, **43**, 1259—1266. Compare Abstr., 1909, i, 48).—Sodium chloroacetate has been substituted for ethyl chloroacetate in the condensations with ethyl 2 : 6-dithiol-4-ketopenthiophen-3 : 5-dicarboxylate, and products similar to those already described have been obtained.

3 : 5-*Dihydroxy*-4-*ketopenthiophendithiophen*,

$$OH\cdot C_4SH<\substack{CO\\ S}>C_4SH\cdot OH,$$

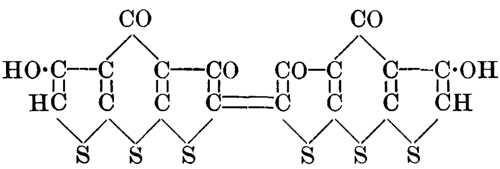
is formed by condensing the dithiol with sodium carbonate, sodium chloroacetate, and a little water for fifteen minutes at 60—70°, then allowing to cool, adding 10N-sodium hydroxide solution, warming to 50°, and finally adding acetic acid. It crystallises in brownish-yellow,

slender needles or in golden-yellow prisms, m. p. 255° (decomp.). The *diacetyl* derivative, $C_{18}H_8O_5S_3$, forms colourless, glistening needles, m. p. 174°.

Ethyl 3-hydroxy-6-thiol-4-ketopenthiophenthiophen-5-carboxylate,

$$\begin{matrix} CO_2Et\cdot C\cdot CO\cdot C—C\cdot OH \\ \quad\| \qquad\quad \| \qquad \| \\ HS\cdot C—S—C\cdot S\cdot CH \end{matrix},$$

is formed when a much smaller amount of sodium chloroacetate is used. It crystallises in orange-red prisms or yellow needles, m. p. 174·5° (decomp.).



Bis-5-hydroxy-4-ketopenthiophendithiophen (annexed formula) is obtained in the form of its mono- or di-potassium salt when the dihydroxyketopenthiophendithiophen is oxidised with ammonium persulphate in potassium hydroxide solution or with potassium ferricyanide. The salts form black, amorphous powders, and when decomposed with mineral acids yield the free compound, $C_{18}H_4O_6S_6$, as a black powder.

Chloroacetone condenses with the dithiol in the same manner as sodium chloroacetate, and it is easy to obtain a theoretical yield of the intermediate product, *ethyl 4-keto-2 : 6-dithiolacetonylpenthiophen-3 : 5-dicarboxylate*, $CO<\begin{matrix}C(CO_2Et):C(S\cdot CHAc)\\C(CO_2Et):C(S\cdot CHAc)\end{matrix}>S$, as glistening, colourless needles, m. p. 77°, which yield *3 : 5-dihydroxy-2 : 6-diacetyl-4-ketopenthiophendithiophen*, $C_9OS_3(OH)_2Ac_2$, when warmed with alkalis. The dihydroxy-compound crystallises in pale yellow needles, which decompose at 300°, and yields a *tri-phenylhydrazone*, $C_{31}H_{26}O_2N_6S_3$, in the form of red plates, decomposing at 261°.

Ethyl 2-acetyl-3-hydroxy-6-thiol-4-ketopenthiophenthiophen-5-carboxylate, $\begin{matrix} CO_2Et\cdot C\cdot CO\cdot CH—C\cdot OH \\ \| \qquad \| \qquad | \\ SH\cdot C—S\cdot CH\cdot S\cdot CAc \end{matrix}$, obtained when a smaller amount of chloroacetone is used, crystallises in orange-yellow needles, m. p. 143—144°.

Bromoacetophenone also condenses with the dithiol, yielding *ethyl 4-ketopenthiophen-2 : 6-dithiolacetophenone-3 : 5-dicarboxylate*,

$$CO<\begin{matrix}C(CO_2Et):C(S\cdot CH_2\cdot COPh)\\C(CO_2Et):C(S\cdot CH_2\cdot COPh)\end{matrix}>S,$$

as pale yellow plates, m. p. 142—143°; with alkalis it yields *3 : 5-dihydroxy-2 : 6-dibenzoyl-4-ketopenthiophendithiophen*,

$$C_9OS_3(OH)_2(COPh)_2,$$

which crystallises in deep yellow plates, m. p. 245°.

Ethyl 2-benzoyl-3-hydroxy-6-thiol-4-ketopenthiophenthiophen-5-carboxylate, $C_{17}H_{12}O_5S_3$, crystallises in orange-red, glistening needles, m. p. 157°. J. J. S.

[Preparation of Halogen "Thioindigos" (Bisoxythionaphthens).] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 219268).—When "6 : 6′-diethoxythioindigo" dissolved in sulphuric acid containing anhydride is treated with bromine, a

"*dibromo*-6 : 6′-*diethoxythioindigo*" is obtained. When chlorine is employed, a "*chloro*-6 : 6′-*diethoxythioindigo*" is formed.

F. M. G. M.

Oxidation Products of "Thioindigo." NEGOITA DANAÏLA (*Bull. Soc. chim.*, 1910, [iv], **7**, 359—361. Compare Abstr., 1908, i, 987; 1909, i, 251).—When "thioindigo," suspended in acetic acid, is oxidised by nitric acid (94%), three *substances* are produced: $C_{16}H_8O_3S_2$, m. p. about 325° (decomp.); $C_{16}H_8O_4S_2$, m. p. 245° (decomp.), and $C_{16}H_8O_5S_2$, m. p. 237° (decomp.). The first crystallises from xylene, and the other two from nitrobenzene. All three are red, and possess properties similar to those of "thioindigo"; they are reduced by sodium hyposulphite and by zinc and acetic acid, forming colourless substances. Their solutions in sulphuric acid are blue or bluish-green, but become reddish-violet for the first two, and orange for the third on dilution. In xylene solution the first shows an absorption band at $\lambda = 539$, the second at $\lambda = 537$, and the third at $\lambda = 487{\cdot}7$. The first and third also show bands at $\lambda = 497{\cdot}5$ and $\lambda = 494$ respectively.

T. A. H.

The Alleged Formation of Adrenaline from Tyrosine. A. J. EWINS and P. P. LAIDLAW (*J. Physiol.*, 1910, **40**, 275—278).—No evidence of the formation of adrenaline from tyrosine or from *p*-hydroxyphenylethylamine and dihydroxyphenylethylamine was found. Halle's experiments in this direction are criticised.

W. D. H.

The Adrenaline Series. CARL MANNICH (*Arch. Pharm.*, 1910, **248**, 127—171. Compare Abstr., 1909, i, 321; this vol., i, 167).—The reaction between methylamine and chloro- or bromo-hydrins of the types: $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH(OH)\cdot CH_2Br$ and

$$C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2Br$$

is more complex than Barger and Jowett (Trans., 1905, **87**, 967) and Pauly and Neukam (this vol., i, 96) suppose. A mere replacement of the halogen by the methylamino-group does not occur. An unstable oxide is first formed, which reacts with a second molecule of methylamine to form bases of the adrenaline series (I) and of the *iso*adrenaline series (II); for example, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2Br \xrightarrow{NH_2Me}$

$$C_6H_3(OMe)_2\cdot CH{<}^{O}_{CH_2} \xrightarrow{NH_2Me} \text{(I) } C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2\cdot NHMe$$

and (II) $C_6H_3(OMe)_2\cdot CH(NHMe)\cdot CH_2\cdot OH$. The constitution of the side-chain is of importance in determining the proportions of the two bases obtained, because *iso*safrolebromohydrin and *iso*eugenol methyl ether bromohydrin yield only the bases of the *iso*-series (II); in these two cases the intermediately formed oxides are stable, and can be isolated. Bases of the *iso*-series can be dealkylated by hydriodic acid, yielding products of very feeble physiological activity. Bases of the adrenaline series are also dealkylated, but at the same time the methylamino-group is displaced, as is the case with adrenaline itself, by treatment with mineral acids. The dibromides of 3 : 4-methylenedioxystyrene, 3 : 4-dimethoxystyrene, and similar substances readily suffer replacement of the α-halogen atom by a methoxy-

group by treatment with boiling methyl alcohol, and the resulting methoxy-bromide reacts with alcoholic methylamine in the sense: $\cdot CH(OMe)\cdot CH_2Br + 2NH_2Me = \cdot CH(OMe)\cdot CH_2\cdot NHMe + NH_2Me,HBr$. Unfortunately, however, the dealkylation of these compounds by hydriodic acid is also accompanied by the elimination of methylamine.

[With P. NEUMANN.]—The following series of reactions lead to a satisfactory yield of 3:4-dimethoxystyrene. Veratrole, which is obtained almost quantitatively from guaiacol and methyl sulphate in alkaline solution, is converted by aluminium chloride and acetyl chloride in carbon disulphide at 0° into acetoveratrone (3:4-dimethoxyacetophenone), b. p. 286—288° or 158°/9 mm. (not 205°/10 mm., as given in the literature), which readily dissolves in ice-water and separates almost completely by warming, and forms an *oxime*, m. p. 140°, and a *semicarbazone*, m. p. 211° (decomp.). Acetoveratrone is reduced by sodium amalgam and alcohol to the *pinacone*,

$$C_6H_3(OMe)_2\cdot CMe(OH)\cdot CMe(OH)\cdot C_6H_3(OMe)_2,$$

m. p. 169°, and by sodium and alcohol to 3:4-*dimethoxyphenylmethyl carbinol*, $C_6H_3(OMe)_2\cdot CHMe\cdot OH$, b. p. 156—160°/9 mm., which forms an *acetate*, b. p. 156—158°/8 mm., and a *chloride*, m. p. 65—67°, from which the *ethyl ether*, $C_6H_3(OMe)_2\cdot CHMe\cdot OEt$, b. p. 132°/8 mm., is obtained by the action of alcoholic sodium ethoxide, and 3:4-dimethoxystyrene by boiling pyridine.

α-3:4-Dimethoxy-β-bromo-α-hydroxyethylbenzene, obtained from 3:4-dimethoxystyrene by Barger and Jowett's method (*loc. cit.*), yields after two to three days' interaction at 0° with 33% alcoholic methylamine a mixture of the two bases (I and II) (above), which is separated by means of the insolubility of the hydrochloride of (II) in acetone. iso*Adrenaline dimethyl ether* (formula II), m. p. 63—64°, crystallises from anhydrous ether, forms a *hydrochloride*,

$$C_{11}H_{17}O_3N,HCl,$$

m. p. 178, and yields by boiling with hydriodic acid, D 1·68, methyl iodide and a viscous liquid, which probably contains *iso*adrenaline, since a very dilute aqueous solution responds to the catechol reaction with ferric chloride. *Adrenaline dimethyl ether* (formula I), m. p. 104°, b. p. 196°/13 mm., separates from ethyl acetate in leaflets, does not yield crystalline salts, and suffers profound degradation by treatment with boiling hydriodic acid, resinous products and methylamine being formed.

3:4-Dimethoxystyrene dibromide and boiling methyl alcohol produce 3:4-*dimethoxy-β-bromo-α-methoxyethylbenzene*,

$$C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2Br,$$

an oily liquid which is decomposed by distillation, yielding ω-bromo-3:4-*dimethoxystyrene*, $C_6H_3(OMe)_2\cdot CH{:}CHBr$, m. p. 65°, and reacts with 33% alcoholic methylamine at 110° for ten hours to form *adrenaline trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NHMe$, b. p. 164—166°/12 mm., the *hydrochloride* of which has m. p. 182°, and the *hydriodide*, m. p. 163—164°. The decomposition of the trimethyl ether by hydriodic acid results in the formation of methyl iodide, methylamine, and resinous products.

3:4-Dimethoxy-β-bromo-α-methoxyethylbenzene reacts in a similar

way with 33% alcoholic dimethylamine to form *N-methyladrenaline trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NMe_2$, b. p. 155—156°/9 mm. (*hydrochloride*, m. p. 175°), and with saturated alcoholic ammonia to form *arterenol trimethyl ether*, $C_6H_3(OMe)_2\cdot CH(OMe)\cdot CH_2\cdot NH_2$, b. p. 164—167°/12 mm. [*hydrochloride*, m. p. 167° (decomp.); *platinichloride*, decomposing at 160°].

[With W. JACOBSOHN.]—The reaction between *iso*eugenol methyl ether bromohydrin and 13% alcoholic methylamine for two days leads to the formation of β-methyl*iso*adrenaline dimethyl ether,

$$C_6H_3(OMe)_2\cdot CH(NHMe)\cdot CHMe\cdot OH,$$

m. p. 63, which forms a *hydrochloride*, m. p. 205°, insoluble in acetone, and is converted by hydriodic acid into β-methyl*iso*adrenaline, $C_6H_3(OH)_2\cdot CH(NHMe)\cdot CHMe\cdot OH$. [These compounds have been described previously as β-methyladrenaline dimethyl ether and β-methyladrenaline respectively (Abstr., 1909, i, 321).] This base, like others of the *iso*-series, is stable to boiling mineral acids, and exhibits very slight physiological activity.

The reaction between 3:4-methylenedioxy-β-bromo-α-hydroxyethylbenzene and 10% alcoholic methylamine for three days leads to the formation of two bases, iso*adrenaline methylene ether*,

$$CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(NHMe)\cdot CH_2\cdot OH,$$

m. p. 81°, the *hydrochloride* of which, m. p. 166—168°, is insoluble in acetone, and *adrenaline methylene ether*,

$$CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OH)\cdot CH_2\cdot NHMe,$$

m. p. 95—96°.

An aqueous alcoholic mixture of the preceding bromohydrin and dimethylamine yields a viscous liquid, b. p. 180—190°/16 mm., which probably consists of a mixture of the two bases,

$$CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OH)\cdot CH_2\cdot NMe_2$$

and $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(NMe_2)\cdot CH_2\cdot OH$, one of which (probably the second), m. p. 88—89°, b. p. 185—186°/16 mm., can be separated as the *hydrochloride*, m. p. 185—186°, from the solution of the mixture in alcohol. The presence of the first base in the mixture is indicated by treating a benzene solution of the liquid with sodium, and subsequently with methyl iodide, at 100° for five hours, whereby a *methiodide*, $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NMe_3I$, m. p. 244° (decomp.), is obtained by repeated crystallisation of the product from alcohol, identical with that described below.

3:4-Methylenedioxystyrene dibromide is converted by boiling methyl alcohol into 3:4-*methylenedioxy-β-bromo-α-methoxyethylbenzene*, $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OMe)\cdot CH_2Br$, b. p. 167—170°/4 mm. (with partial decomp.), which is converted by 33% alcoholic methylamine at 110° for ten hours into the *methyl ether* of adrenaline methylene ether, $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NHMe$, b. p. 175—178°/25 mm.

(*hydrochloride*, m. p. 159—160°), and by 33% alcoholic dimethylamine in a similar manner into the *methyl ether* of *N*-methyladrenaline methylene ether, $CH_2<^O_O>C_6H_3\cdot CH(OMe)\cdot CH_2\cdot NMe_2$, b. p. 150°/16 mm. (*hydrochloride*, m. p. 206°). By the addition of methyl iodide to the latter base, a *methiodide*, m. p. 244° (decomp.), is obtained, identical with that mentioned above.

A base, probably *β-methyl*iso*adrenaline methylene ether*,

$$CH_2O_2{:}C_6H_3\cdot CH(NHMe)\cdot CHMe\cdot OH,$$

m. p. 66°, b. p. 186°/17 mm. [*hydrochloride*, m. p. 225—226° (decomp.)], is obtained by shaking *β*-bromo-*a*-hydroxydihydro*iso*safrole and aqueous methylamine for fifty hours or by heating *iso*safrole oxide and 33% alcoholic methylamine at 100° for six hours. *Nβ-Dimethyl*iso*adrenaline methylene ether*, $CH_2O_2{:}C_6H_3\cdot CH(NMe_2)\cdot CHMe\cdot OH$, m. p. 66—68°, b. p. 175—176°/15 mm. (*hydrochloride*, m. p. 212°), is obtained by the interaction of the preceding *iso*safrole bromohydrin and 33% alcoholic dimethylamine in aqueous alcohol for two days at the ordinary temperature.

β-Bromo-*a*-methoxydihydro*iso*safrole (Hoering, Abstr., 1905, i, 903) and 33% alcoholic methylamine, reacting at 120° for six hours, yield the *methyl ether* of *β*-methyladrenaline methylene ether,

$$CH_2O_2{:}C_6H_3\cdot CH(OMe)\cdot CHMe\cdot NHMe,$$

b. p. 159—160°/14 mm., the *hydrochloride* of which has m. p. 202° (decomp.). C. S.

Angostura Alkaloids. JULIUS TROGER and O. MÜLLER (*Arch. Pharm.*, 1910, **248**, 1—22. Compare Beckurts and Frerichs, Abstr., 1906, i, 34).—Extr. angostur. æther (Merck) is mixed with its own volume of ether, and repeatedly treated with 20% acetic acid until the aqueous layer is only faintly yellow. The aqueous extracts are treated with concentrated sulphuric acid so long as sulphates are precipitated. These are collected, the bases are liberated by ammonium hydroxide, and are recrystallised from alcohol until the m. p. is 95°. The product is then separated by petroleum into an insoluble basic mixture *A*, and a solution from which cusparine and a fraction, m. p. 106—150°, are obtained.

The filtrate from the sulphates yields with concentrated hydrochloric acid a yellow salt, from which a base, probably galipidine, is isolated. The hydrochloric acid filtrate is basified with ammonium hydroxide, the reddish-brown, viscous product is treated with dilute sulphuric acid, the resulting sulphates are purified by crystallisation, and the liberated bases are recrystallised from alcohol, whereby galipine is obtained in a good yield.

The basic mixture *A* is separated by alcohol into cusparine, galapine, and a new, very sparingly soluble alkaloid, m. p. 233°.

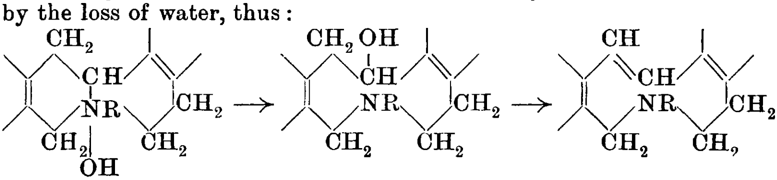
The ethereal solution of the original extract, after its treatment with 20% acetic acid, is repeatedly extracted with dilute sulphuric acid; the bases are liberated from the acid extracts, and are purified from petroleum, whereby a good yield of cusparine is obtained.

Galipine, $C_{20}H_{21}O_3N$, m. p. 115—115·5°, contains three methoxy-

groups, and yields veratric and anisic acids, a small quantity of an amine, and an acid, m. p. 241—247°, containing nitrogen (cinchomeronic acid?) by oxidation with potassium dichromate and sulphuric acid; the oxidation of galipine sulphate by potassium permanganate in neutral solution at 40—50° yields a very small amount of veratric acid, an *acid*, $C_8H_7O_6N$, m. p. 244—246°, and another acid containing nitrogen, m. p. 262—264°. When the oxidation of the galipine sulphate by potassium permanganate is not carried to completion, but is interrupted when all the galipine has been oxidised, the products of oxidation are found to consist of veratric acid, together with acids, m. p. 191·5°, 165—166°, 188—189·5°, the amounts of which are too small for their satisfactory examination.

The oxidation of galipidine by potassium dichromate and sulphuric acid yields a mixture of two aromatic acids (one of which probably is veratric acid), a base, m. p. 138°, formic acid, and a liquid with the odour of pyridine; the available amount of galipidine, however, was too small for the satisfactory examination of these products. C. S.

Isomerism of the Ammonium Compounds Derived from Tetrahydroberberine. ARTHUR VOSS and JULIUS GADAMER (*Arch. Pharm.*, 1910, **248**, 43—80).—The recognition of berberine as an *iso*quinoline derivative makes it permissible to conceive that the strongly basic ammonium hydroxides obtained by the action of silver oxide on tetrahydroberberine alkyl iodides may undergo transformation into feebly basic carbinol bases, from which anhydro-bases could result by the loss of water, thus:



The hydroxyl group of the ammonium base can evidently migrate to any one of the three neighbouring carbon atoms, but the depicted formula of the carbinol base is the only one that accounts for the production of an optically inactive anhydro-base. The carbinol base has not been isolated; the authors show, however, that the theory serves to reconcile many of the conflicting observations of Schmidt and his co-workers on the alkyl iodide additive compounds of tetrahydroberberine.

Tetrahydroberberine contains an asymmetric carbon atom, and also a neighbouring nitrogen atom, which is attached to three different groups. By the addition of an alkyl iodide, therefore, two diastereoisomeric quaternary iodides should result. This is the case, for *d*- and *l*-canadines (the resolution products of tetrahydroberberine) yield each a pair of ethiodides, d-*a-canadine ethiodide*, $C_{22}H_{26}O_4NI,1\frac{1}{2}H_2O$, m. p. 187°, $[\alpha]_D^{20}$ $+92·2°$ in alcohol, and d-*β-canadine ethiodide*, m. p. 225°, $[\alpha]_D^{20}$ $+115·0°$, and the corresponding l-*a-compound*, m. p. 187°, $[\alpha]_D^{20}$ $-91·5°$, and l-*β-compound*, m. p. 225°, $[\alpha]_D^{20}$ $-115·3°$. r-*a-Canadine ethiodide*, $C_{22}H_{26}O_4NI,\frac{1}{2}H_2O$, has m. p. 187°, and the r-*β-compound*, $C_{22}H_{26}O_4NI,1\frac{1}{2}H_2O$, has m. p. 240°; a mixture of equal quantities

of the two substances, after being crystallised from 70% alcohol, is identical with tetrahydroberberine ethiodide, m. p. 229—230°. The *a-canadine ethochlorides* crystallise in small, yellow crystals containing $2H_2O$, and have m. p. 233°; the *d*-form has $[\alpha]_D^{20}$ +128·3°, and the *l*-form has $[\alpha]_D^{20}$ −127·3°; the racemic modification also has m. p. 233°. The *β-canadine ethochlorides,* m. p. 245°, contain $2H_2O$; the *d*-form has $[\alpha]_D^{20}$ +138·5°, and the *l*-form, $[\alpha]_D^{20}$ −138·8°; the racemic modification has m. p. 260°. The corresponding *ethonitrates* are also described. The α-compounds are converted into the β-compounds by heating in the absence of air.

The action of silver oxide on tetrahydroberberine ethiodide in 50% alcohol, or of barium hydroxide on *tetrahydroberberine ethyl hydrogen sulphate,* m. p. 270°, yields the corresponding ammonium base, which, however, cannot be isolated free from the carbonate.

The *ethyl anhydro-base* of tetrahydroberberine, $C_{20}H_{20}O_4NEt$, m. p. 132·5°, is obtained by heating tetrahydroberberine ethyl carbonate in hydrogen for seventeen and a-half hours, treating the solution of the product in very dilute hydrochloric acid with ammonium hydroxide, and extracting the precipitate with ether; it has only a slight alkaline reaction, is reconverted into the quaternary ammonium base by boiling alcohol, and forms a *hydrochloride,* m. p. 185°, *nitrate,* m. p. 165—166°, and *hydrogen sulphate,* m. p. 260°.

l-α- and β-Canadine methiodides, obtained from *l*-canadine and an excess of ethyl iodide, are converted, in alcoholic solution, into the hydroxides; the solution is evaporated in a current of hydrogen, the residue is dissolved in dilute hydrochloric acid, and the solution, after treatment with ammonium hydroxide, is extracted with ether; the residue obtained from the ethereal solution is purified from acetone, and consists of the anhydro-base, m. p. 132·5°, which is quite inactive optically. The ammoniacal mother liquor contains β-tetrahydroberberine ethochloride, m. p. 257°, which appears to be identical with *r*-β-canadine ethochloride, and also with Link's tetrahydroberberine ethochloride (Abstr., 1892, 1499); the nitrates of the three bases also correspond. C. S.

Nature of the So-called Double Salts formed by Caffeine with Alkali Salts. GIOVANNI PELLINI (*Atti R. Accad. Lincei,* 1910, [v], **19**, i, 329—333).—In order to ascertain whether the substances obtained by dissolving caffeine in concentrated aqueous solutions of salts of the alkali metals and evaporating the liquid to dryness at a gentle heat are definite double salts or merely mixtures, the author has investigated the mutual solubility relations of caffeine and sodium benzoate. The solubility of caffeine in water is increased considerably by the addition of the benzoate, which also exhibits increased solubility, but to a less degree. The solubility curves at 25° and at 40° indicate that these two compounds do not unite to form a compound capable of existence in the solid state. T. H. P.

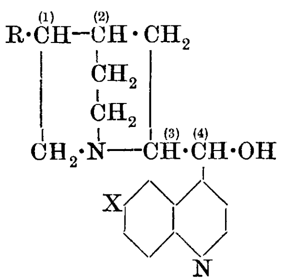
Existence in Solution of Compounds of Caffeine and Sodium Benzoate. GIOVANNI PELLINI and MARIO AMADORI (*Atti R. Accad. Lincei,* 1910, [v], **19**, i, 333—338. Compare preceding abstract).—The authors have measured the variations produced in the freezing

points of solutions of sodium benzoate of a number of different, fixed concentrations by the addition of increasing quantities of caffeine. With all the sodium benzoate solutions, abnormal changes in the freezing point were observed. With the more dilute solutions, the presence of caffeine lowers the freezing point, but by less than the calculated amount; in the case of solutions of medium concentration, the freezing points are not changed, whilst with more concentrated solutions, rises of the freezing points are produced by addition of caffeine. It is hence evident that in solution caffeine and sodium benzoate form a compound (probably by the union of the caffeine with the benzoic ion to form a complex caffeinebenzoic ion) which undergoes dissociation in dilute solution.

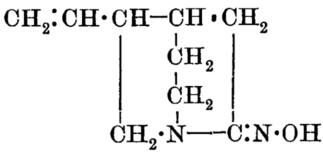
The addition of mannitol, dextrose, or aniline to solutions of sodium benzoate produces normal depressions of the freezing points.

T. H. P.

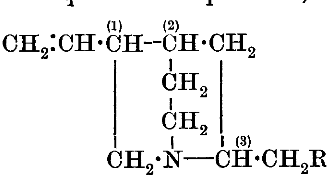
Cinchona Alkaloids. XII. Paul Rabe [with Erich Kuliga, Oswald Marschall, Wilhelm Naumann, and William F. Russell] (*Annalen*, 1910, **373**, 85—120. Compare Abstr., 1909, i, 252, 407, 408).—The configurations of cinchonine, cinchonidine, quinine, quinidine, and hydrocinchonine may be represented by the annexed formula; in the first two alkaloids, R = $-CH{:}CH_2$ and X = H; in quinine and quinidine, R = $-CH{:}CH_2$ and X = OMe; in hydrocinchonine, R = Et and X = H; for the purpose of discussing the stereochemical relationship of these alkaloids, the four asymmetric carbon atoms are numbered in the manner indicated.



It has been shown (*loc. cit.*) that cinchonine and cinchonidine when oxidised yield cinchoninone, whilst quinine and quinidine give rise to quininone; these two ketones are decomposed when acted on by amyl nitrite, yielding α-oximino-β'-vinylquinuclidine (annexed formula); it is now found that the preparations of this substance from the four alkaloids are optically identical, showing that these alkaloids with regard to the carbon atoms (1) and (2) have the same spacial configuration; the same arrangement is probably present also in hydrocinchonine.



The deoxy-bases derived from cinchonine and cinchonidine, likewise from quinine and quinidine, are structurally identical, but differ from one another in optical properties; since there are three asymmetric carbon atoms present in the molecule of these compounds (annexed formula), of which the spacial arrangement of (1) and (2) in each case has been shown to be identical, it follows that the isomerism results from the different arrangement of the substituents on (3); consequently, the isomerism of cinchonine and cinchonidine, likewise of



quinine and quinidine, must also be occasioned by the mirror-image arrangement of the substituents on the carbon atom (3).

The formation of cinchotoxine (cinchonicine) from cinchonine and cinchonidine is accompanied by the destruction of the asymmetry of the carbon atoms (3) and (4); hence the formation of the same compound from the stereo-isomerides. Similarly, quinine and quinidine give rise to only one compound, namely, quinotoxine (quinicine).

The reason why only one ketone is obtained from quinine and quinidine, also from cinchonine and cinchonidine, has been discussed already (compare Abstr., 1909, i, 252); the present communication contains the results of a careful investigation of the mutarotation of quininone and cinchoninone.

Measurements of the optical rotatory powers of solutions of the cinchona alkaloids are cited, which show that they do not change with time. The following values of $[\alpha]_D$ are recorded; unless otherwise stated, the solvent is 99% alcohol: cinchonine, $[\alpha]_D^{23}$ $+224°$ ($c = 0·606$ at 20°); cinchonine hydrochloride, $[\alpha]_D^{25}$ $+133°$ ($c = 1·407$ at 20° in chloroform); cinchonidine, $[\alpha]_D^{11}$ $-111°$ ($c = 0·878$); quinine, $[\alpha]_D^{15}$ $-158°$ ($c = 2·136$ at 15°); quinidine, $[\alpha]_D^{15}$ $+243·5°$ ($c = 0·7735$ at 15°); hydrocinchonine, $[\alpha]_D^{14}$ $+190°$ ($c = 0·406$ at 12°); cinchonine chloride ($2H_2O$), $[\alpha]_D^{13}$ $+49·77°$ ($c = 2·009$), anhydrous, m. p. 110°, $[\alpha]_D^{13}$ $+55·7°$ ($c = 1·975$); cinchonine chloride hydrochloride, $[\alpha]_D^{24}$ $+49·5°$ ($c = 1·5555$ in water); cinchonidine chloride, $[\alpha]_D^{13}$ $+78·2°$ ($c = 2·020$); cinchonidine chloride hydrochloride, $[\alpha]_D^{24}$ $+24·16°$ ($c = 1·573$ in water); quinine chloride, $[\alpha]_D^{15}$ $+60·36°$ ($c = 1·9465$); quinidine chloride, $[\alpha]_D^{15}$ $+35·25°$ ($c = 1·943$); deoxycinchonine, $[\alpha]_D^{13}$ $+179·3°$ ($c = 2·025$), $+194·3°$ ($c = 2·030$ in chloroform); deoxycinchonidine, $[\alpha]_D^{13}$ $-29·9°$ ($c = 2·006$), $-19·7$ ($c = 2·006$ in chloroform); deoxyquinine ($2H_2O$), $[\alpha]_D^{15}$ $-93·0°$ ($c = 2·252$), anhydrous, $[\alpha]_D^{20}$ $-97·7°$ ($c = 2·021$); deoxyquinidine ($2H_2O$), $[\alpha]_D^{15}$ $+191·9°$ ($c = 2·254$), anhydrous, $[\alpha]_D^{20}$ $+211·1°$ ($c = 2·023$); oximinovinylquinuclidine, $[\alpha]_D^{16}$ $+113°$ ($c = 2·005$).

Although cinchotoxine (cinchonicine) contains the group $-CH_2·CO-$, it does not exhibit mutarotation; $[\alpha]_D^{18}$ $+49·62°$ ($c = 2·684$ at 20°). The following values refer to the rotation of the solution when equilibrium has been established: cinchoninone, $[\alpha]_D^{20}$ $+76·1°$ ($c = 3·302$), $+76·9°$ ($c = 1·652$); various specimens of cinchoninone hydrochloride were found to differ in the initial optical rotatory power, but all gave the final value $[\alpha]_D^{14}$ $+66·4°$ ($c = 1·656$ in water), $+166·6°$ ($c = 1·656$ in chloroform); quininone, $[\alpha]_D^{20}$ $+75·5°$ ($c = 2·000$); hydrocinchoninone, $[\alpha]_D^{20}$ $+76·4°$ ($c = 2·296$). W. H. G.

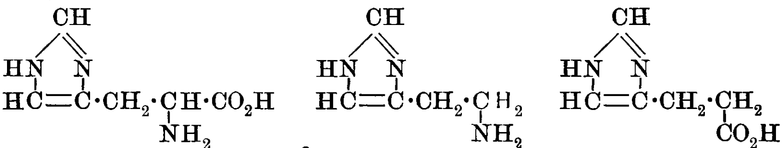
Solubility of Alkaloids of Cinchona Bark and their Salts in Water at 25°. GEORGE L. SCHAEFER (*Amer. J. Pharm.*, 1910, **82**, 175—178).—The solubilities of quinine, cinchonidine, cinchonine, and quinidine and of a large number of their salts are given. The results were obtained by determining the parts of water at 25° necessary to dissolve one part of the alkaloid or salt, in order to avoid the difficulty due to the decomposition of the salt by the action of water.

T. A. H.

Corydalis Alkaloids. JOHANNES GADAMER (*Arch. Pharm.*, 1910, **248**, 204—206).—With the acceptance of Dobbie and Lauder's

formula for corydaline (Trans., 1902, **81**, 148), the author considers that the study of the chemistry of the corydaline sub-group of the corydalis alkaloids may now be replaced by that of the corycavine and bulbocapnine sub-groups (Abstr., 1905, i, 462). He has already proved that bulbocapnine, corydine, and corytuberine contain the ring system of *apo*morphine, and has converted corytuberine into corydine. C. S.

Bacterial Cleavage of Histidine D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1910, **65**, 504—510).—If histidine undergoes anaërobic bacterial cleavage due to the addition of a little putrefying pancreas, the product obtained may be β-iminazolylethylamine if carbon dioxide is split off; the obtaining of this substance proves that the amino-group of histidine is in the α-position to the carboxyl group, a point previously uncertain. It also may undergo the change into iminazolylpropionic acid.



Histidine. β-Iminazolylethylamine. Iminazolylpropionic acid.

W. D. H.

Nupharine. A. GORIS and L. CRÉTÉ (*Bull. Sci. Pharm.*, 1910, Jan., Reprint, 3 pp.).—This alkaloid, $C_{18}H_{24}O_2N_2$, was first isolated by Grüning (Abstr., 1883, 369) from the rhizomes of *Nuphar luteum*, in the form of a colourless, sticky mass, which became syrupy at 65°. The authors have isolated the alkaloid from the same source by extraction with dilute hydrochloric acid, precipitation with silicotungstic acid, and decomposition of this precipitate with barium hydroxide. They found that the alkaloid when left in contact with barium hydroxide was slowly decomposed, yielding cinnamaldehyde, which was identified by the blood-red coloration which it produced with β-naphthol and sulphuric acid dissolved in alcohol (compare Deniges, *Bull. Soc. Pharm. Bordeaux*, 1908, **48**, 267). T. A. H.

Morphine Series. I. Ethylthiocodides. ROBERT PSCHORR and A. ROLLETT (*Annalen*, 1910, **373**, 1—14).—The replacement of the bromine atom in bromocodide by hydroxyl, under suitable conditions, gives rise to three isomerides of codeine (compare Schryver and Lees, Trans., 1900, **77**, 1024; 1901, **79**, 563, 1408; Knorr and Hörlein, Abstr., 1907, i, 151, 956). Similarly, it is found that four isomeric ethylthiocodides may be obtained by replacing the bromine atom by the –SH group (compare Pschorr, Abstr., 1906, i, 877). The α-compound is formed by the action of ethyl mercaptan and aqueous sodium hydroxide on α-bromocodide at 100°; it is converted by an alcoholic solution of sodium ethoxide into the β-isomeride, which may also be prepared, therefore, by the action of an alcoholic solution of sodium ethoxide and ethyl mercaptan on α-bromocodide; a small quantity of a third γ-isomeride is formed in the latter case. The

δ-compound results from the action of ethyl mercaptan and sodium ethoxide on α-chlorocodide; β-chlorocodide gives rise to the same compounds as bromocodide.

An account of the chemical properties of β-ethylthiocodide, which differs in a marked degree from the other isomerides in reactivity, is given in a separate paper (compare following abstract). The α-, γ-, and δ-isomerides behave quite normally; they combine with methyl iodide, yielding methiodides, which are converted by aqueous alkalis into the corresponding ethylthiomethylmorphimethines. α-Ethylthiomethylmorphimethine, in analogy to the α- and γ-methylmorphimethines from codeine and *iso*codeine, is converted by sodium ethoxide into the β-isomeride, whilst the γ- and δ-ethylthiomethylmorphimethines, in analogy to the ε- and ζ-methylmorphimethines from ψ-codeine, are not altered by this reagent.

The degradation of the ethylthiomethylmorphimethines by Hofmann's reaction leads to the formation of known basic compounds and oily, nitrogen-free substances, except in the case of the δ-isomeride, which decomposes into trimethylamine and a crystalline vinyl compound.

α-Chlorocodide passes into β-chlorocodide when heated for a short time at 155—157° (compare Knorr and Hörlein, Abstr., 1908, i, 41); bromocodide does not undergo a similar rearrangement when heated.

α-*Ethylthiocodide*, $C_{20}H_{25}O_2NS$, crystallises in glistening rods, m. p. 88—89°, $[\alpha]_D^{20}$ −340° (in alcohol); the *hydriodide* forms glistening leaflets, m. p. 217° (corr.); the *methiodide*, $C_{20}H_{25}O_2NS,MeI$, decomposes at 236—237° (corr.), $[\alpha]_D^{20}$ −232·6° (in water). α-*Ethylthiomethylmorphimethine* is an oil; the *hydriodide*, $C_{21}H_{27}O_2NS,HI$, crystallises in glistening leaflets, decomposes at 204—206° (corr.), and has $[\alpha]_D^{20}$ −218·5° (in water); it may also be prepared by the action of ethyl mercaptan and aqueous sodium hydroxide on bromocodide methiodide; the *methiodide*, $C_{21}H_{27}O_2NS,MeI$, crystallises in slender needles, decomposes at 235—236° (corr.), and has $[\alpha]_D^{20}$ −183° (in water). The α-base is converted by *N*-sodium hydroxide solution into β-*ethylthiomethylmorphimethine*, $C_{21}H_{27}O_2NS$, which crystallises in yellow leaflets, m. p. 173—174° (corr.); the same compound is formed by the action of ethyl mercaptan and sodium ethoxide on bromocodide methiodide or chloromethylmorphimethine hydrochloride; the *methiodide* crystallises in needles and decomposes at 124—125° (corr.).

β-Ethylthiocodide has been mentioned previously (compare Pschorr, *loc. cit.*); it crystallises in prisms, m. p. 148°.

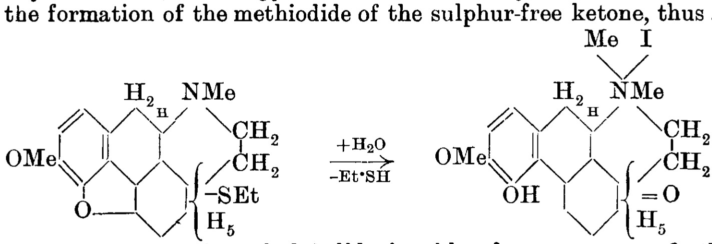
γ-*Ethylthiocodide* is an oil; the *methiodide* crystallises in small, glistening rods, and decomposes at 265—266°, $[\alpha]_D^{20}$ −119·2° (in water). γ-*Ethylthiomethylmorphimethine* is an oil; the *hydriodide* crystallises in leaflets, m. p. 179—180° (corr.), $[\alpha]_D^{20}$ −161° (in water).

δ-*Ethylthiocodide* is an oil, which slowly solidifies when kept; the *hydriodide* decomposes at 255° (corr.), $[\alpha]_D^{20}$ +51·4° (in water); the *methiodide* crystallises from water in prisms, decomposes at 230—234°, and has $[\alpha]_D^{20}$ +55° (in water); it also crystallises with 1Et·OH, and then has m. p. 143—145° (corr.). δ-*Ethylthiomethylmorphimethine* is an oil; the *hydriodide* crystallises in prisms, m. p. 196—197° (corr.), $[\alpha]_D^{20}$ +49° (in water); the *methiodide* forms small rods, m. p. 193—195° (corr.), $[\alpha]_D^{20}$ +39° (in water), and when boiled with *N*-sodium hydroxide solution yields trimethylamine and *ethylthiovinyltetrahydromorphenol*

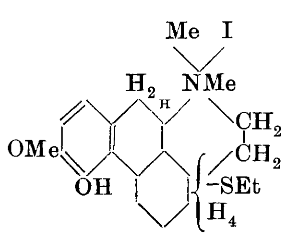
methyl ether, $C_{19}H_{20}O_2S$, which crystallises in prisms, m. p. 97—100°, $[\alpha]_D^{20}$ +689° (in alcohol). W. H. G.

Morphine Series. II. β-Ethylthiocodide. ROBERT PSCHORR (*Annalen*, 1910, **373**, 15—44. Compare preceding abstract).—β-Ethylthiocodide, when acted on by cold dilute hydrochloric acid for a short time, yields a sulphur-free compound, which is both phenolic and ketonic in character, and an ethyl mercaptan additive product of β-ethylthiocodide, thus: $2C_{18}H_{20}O_2N\cdot SEt + H_2O = C_{18}H_{21}O_3N + C_{18}H_{21}O_2N(SEt)_2$; an equivalent mixture of these two substances, when heated with hydrochloric acid, yields a substance containing sulphur, which is both phenolic and ketonic in character, and is also formed directly from β-ethylthiocodide by the action of hot hydrochloric acid: $C_{18}H_{21}O_3N + C_{18}H_{21}O_2N(SEt)_2 + H_2O = 2C_{18}H_{22}O_3N\cdot SEt$. The two ketones are readily converted one into the other; the sulphur-free ketone is extracted almost quantitatively by means of chloroform from an alkaline solution of the ketone containing sulphur, whilst an alkaline solution of the sulphur-free ketone in the presence of ethyl mercaptan, when treated with ammonium carbonate, yields the ketone containing sulphur. The transformation of β-ethylthiocodide into the ketone containing sulphur is accompanied by the migration of the ethylthiol group; this is demonstrated by the following series of changes: β-methylthiocodide, when warmed with hydrochloric acid, yields a ketone which contains the methylthiol group and combines with ethyl mercaptan, yielding a compound, $SMe\cdot C_{18}H_{21}O_2N\cdot SEt$; the latter substance, however, is not identical with the dimercaptyl compound formed from β-methylthiocodide, thus: $C_{18}H_{20}O_2N\cdot SMe + Et\cdot SH = SMe\cdot C_{18}H_{21}O_2N\cdot SEt$, but with that derived by similar means from β-ethylthiocodide and methyl mercaptan.

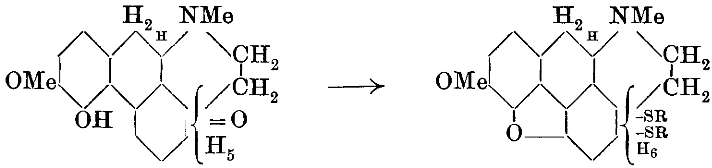
The action of an aqueous-alcoholic solution of methyl iodide on β-ethylthiocodide, in analogy to the action of hot hydrochloric acid, leads to the formation of the methiodide of the sulphur-free ketone, thus:



A cold solution of methyl iodide in chloroform converts β-ethylthiocodide into a compound having the annexed formula; when treated with acetic anhydride, it yields an acetyl derivative identical with the methiodide of the compound obtained by heating β-ethylthiocodide with acetic anhydride. The acetyl compound formed by the action of acetic anhydride on β-ethylthiocodide, when warmed with alkalis, is reconverted into β-ethylthiocodide; the regeneration of the oxygen-bridge which occurs in the



last case also takes place in the formation of the dimercaptyl compound by the action of mercaptan on the ketone, thus:



[With KRECH.]—*β-Ethylthiocodide hydrochloride*, $C_{20}H_{25}O_2NS,HCl$, crystallises in prisms; when treated with cold *N*-hydrochloric acid solution for eighteen hours, it yields (1) *diethyldithiocodide*, the *methiodide* of which, $C_{22}H_{31}O_2NS_2,MeI$, forms glistening leaflets, m. p. 140—150°, and (2) a *ketone*, $C_{18}H_{21}O_3N$, which crystallises in prismatic plates, m. p. 145—147°, $[\alpha]_D^{20}$ $-42.5°$ (in alcohol), and is also formed by boiling *β*-ethylthiocodide with hydrochloric acid; the *hydriodide*, $C_{18}H_{21}O_3N,HI,H_2O$, forms fan-shaped aggregates of small rods, melts at 165°, becomes solid subsequently, and decomposes finally at 265°; the *methiodide* crystallises in leaflets, decomposes at 251°, and yields an *acetate*, $C_{21}H_{26}O_4NI$, which crystallises in needles and decomposes at 269°; the *oxime*, $C_{18}H_{22}O_3N_2$, crystallises in leaflets, decomposes at 175—177°, and yields a *hydrochloride*, which forms needles decomposing at 282—283°; the *semicarbazone*, $C_{19}H_{24}O_3N_4$, crystallises in slender rods and decomposes at 247—248°.

The *ketone*, $C_{20}H_{27}O_3NS$, crystallises with $1H_2O$ in leaflets and small rods, m. p. 121—127°; the anhydrous substance has m. p. 182°; the *hydriodide* forms slender, matted needles and decomposes at 222—223° (corr.); the *methiodide* crystallises in glistening needles and decomposes at 241° (corr.); the *oxime*, $C_{20}H_{28}O_3N_2S$, forms tufts of small rods, m. p. 258° (corr.).

β-Ethylthiocodide interacts with methyl mercaptan in dilute hydrochloric acid, yielding a *substance*, $C_{21}H_{29}O_2NS_2$, which crystallises with 1Me·OH in small plates, m. p. 71—73°; the *methiodide* forms glistening leaflets, $[\alpha]_D^{20}$ $+24.0°$ (in water), and decomposes at 146—147°.

β-Methylthiocodide, $C_{19}H_{23}O_2NS$, prepared from bromocodide and methyl mercaptan, crystallises in prisms, m. p. 124—125°, and interacts with ethyl mercaptan, yielding a *substance*, $C_{21}H_{29}O_2NS_2$, which crystallises in prisms, m. p. 112—115°, and forms a *methiodide*, leaflets decomposing at 184°, $[\alpha]_D^{20}$ $+33.6°$ (in water); a *ketone*, $C_{19}H_{25}O_3NS$, is formed by heating *β*-methylthiocodide with dilute hydrochloric acid; it crystallises in prisms, m. p. 141—142°.

The *compound*, $C_{20}H_{25}O_2NS,MeI$, formed by the action of a cold solution of methyl iodide in chloroform on *β*-ethylthiocodide, crystallises in rectangular prisms and decomposes at 232°; the *acetate*, $C_{23}H_{30}O_3NIS$, crystallises in needles, m. p. 161°; the parent substance is converted by a strong aqueous solution of sodium hydroxide into the corresponding *betaine*, $C_{21}H_{27}O_2NS$, slender needles, m. p. 170—172°, which is converted by (1) a boiling alcoholic solution of methyl iodide into the *methiodide* of the *methyl ether*, $C_{22}H_{30}O_2NSI$, crystallising with 1Et·OH in leaflets, m. p. 209—211° (corr.); (2) an alcoholic solution of methyl iodide under pressure at 100° into a

substance, $C_{20}H_{26}O_3NI$, which contains two methoxy-groups and crystallises in plates, m. p. 260°; the betaine is converted by hot aqueous alkali into β-ethylthiomethylmorphimethine (compare preceding abstract).

ψ-Codeinone interacts with ethyl mercaptan in dilute hydrochloric acid yielding a *substance*, the *methiodide* of which, $C_{20}H_{25}O_3NS,MeI$, crystallises with 1Me·OH in leaflets, m. p. 204° (decomp., corr.), and is soluble in alkalis. W. H. G.

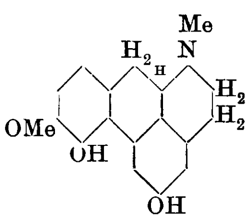
Morphine Series. III. Ethylthiomorphides. ROBERT PSCHORR and GERH. HOPPE (*Annalen*, 1910, **373**, 45—50).—Bromomorphine reacts with ethyl mercaptan, yielding ethylthiomorphides analogous to the ethylthiocodides (compare preceding abstracts).

β-Ethylthiomorphide, $C_{19}H_{23}O_2NS$, is a crystalline substance, decomposes at 200—202°, and is converted (1) by cold dilute hydrochloric acid into *diethyldithiomorphide*, $C_{21}H_{29}O_2NS_2$, small prisms decomposing at 252°, and a *ketone*, $C_{17}H_{19}O_3N$, leaflets decomposing at 215—217°; (2) by 10% hydrochloric acid at a moderate temperature into a *ketone*, $C_{19}H_{25}O_3NS$, slender needles decomposing at 205—208°, the *hydrochloride* of the *oxime* of which, $C_{19}H_{26}O_3N_2S,HCl$, crystallises with $1H_2O$; and (3) by boiling with 10% hydrochloric acid into the ketone, $C_{17}H_{19}O_3N$, already described; the *oxime* of the latter substance decomposes at 260°, and yields a *hydrochloride*, $C_{17}H_{28}O_3N_2,HCl,H_2O$; the ketone is converted by acetic anhydride into a crystalline *diacetyl* derivative, the *methiodide* of which, $C_{21}H_{23}O_5N,MeI$, decomposes at 255—258°.

β-Ethylthiomorphide, when warmed with acetic anhydride and sodium acetate, yields an amorphous *diacetyl* compound, the *methiodide* of which, $C_{23}H_{27}O_4NS,MeI$, crystallises with 1Et·OH, in needles decomposing at 153°.

An *ethylthiomorphide*, crystallising in leaflets decomposing at 180°, was also obtained. W. H. G.

Morphine Series. IV. Constitution of Morphothebaine and Thebenine. ROBERT PSCHORR (*Annalen*, 1910, **373**, 51—74. Compare Pschorr and Massaciu, Abstr., 1904, i, 767; Knorr and Pschorr, Abstr., 1905, i, 814).—[With HANS RETTBERG.]—1. *Morphothebaine.*—It is very probable that morphothebaine has the annexed



formula, since it closely resembles *apo*morphine in properties, and is formed from thebaine, presumably, without migration of the oxygen atoms. It has been found possible to obtain a tetramethoxyphenanthrene from morphothebaine, which, if the latter compound has the constitution given, must contain the methoxy-groups in the 1 : 3 : 5 : 6-positions; the synthesis of 1 : 3 : 5 : 6-tetramethoxyphenanthrene has been undertaken in order to decide this point.

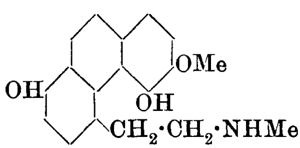
The silver salt of the trimethoxyphenanthrenecarboxylic acid derived from morphothebaine (compare Knorr and Pschorr, *loc. cit.*), when

heated at 250—280° under a pressure of 12 mm., yields a *trimethoxyphenanthrene*, the *picrate* of which, $C_{17}H_{16}O_3,C_6H_3O_7N_3$, has m. p. 104—120°. The *methyl* ester of the acid, $C_{19}H_{18}O_5$, crystallises in yellow, slender needles, m. p. 101—102°; the *ethyl* ester forms glistening leaflets, m. p. 83—84°; the *hydrazide*, $C_{18}H_{18}O_4N_2$, formed by the action of hydrazine hydrate on an alcoholic solution of the ester, crystallises in long, colourless needles, m. p. 176—177°, and is converted by amyl nitrite and an alcoholic solution of hydrogen chloride into the corresponding yellow *azoimide*, which, when heated with alcohol, passes into the corresponding *urethane* derivative, $C_{20}H_{21}O_5N$, long, pale pink needles, m. p. 137—138°. The latter substance is decomposed by a 10% alcoholic solution of ammonia at 150°, yielding *aminotrimethoxyphenanthrene*, the *hydrochloride* of which,

$$C_{17}H_{17}O_3N,HCl,$$

crystallises in long needles and decomposes at 250°; the amino-compound is converted through the diazo-derivative into the corresponding *hydroxy*-compound, which when methylated with methyl sulphate yields *tetramethoxyphenanthrene*, $C_{18}H_{18}O_4$, crystallising in flat, glistening needles, m. p. 108—109°; the *picrate* forms small, dark red needles, m. p. 147—148°.

[With HEINRICH LOEWEN.]—II. *Thebenine.*—The annexed constitutional formula is assigned to thebenine for the following reasons:



(1) The trimethoxyphenanthrenecarboxylic acid, obtained by Pschorr and Massaciu from thebenine (*loc. cit.*), when heated yields 3 : 4 : 8-trimethoxyphenanthrene (compare Pschorr, Abstr., 1900, i, 233). (2) The methoxy-group must occupy position 3, since thebenine may be obtained from codeinone (compare Knorr and Hörlein, Abstr., 1907, i, 547), which contains a methoxy-group in position 3. (3) The $-C\cdot C\cdot N$ side-chain occupies position 5, since it readily undergoes ring-condensation with the hydroxyl group in position 4 with the formation of thebenol. It is definitely shown that the hydroxyl group in position 4 takes part in the formation of the new ring, since ethebenine also undergoes ring condensation, yielding ethebenol (compare Freund, Abstr., 1897, i, 495; 1899, i, 307), and the ethoxy-group in ethebenine is situated at 8, because it gives rise to 3:4-dimethoxy-8-ethoxyphenanthrene (compare following abstract).

Ethebenine is converted by sodium hydroxide and methyl sulphate into the *methosulphate* of *methethebenine*, $C_{24}H_{33}O_7NS$, which crystallises in slender needles, m. p. 241° (corr.); the corresponding *methiodide*, $C_{21}H_{27}O_3N,MeI$, has m. p. 252° (corr.). The methosulphate, when heated with alcoholic potassium hydroxide, yields 3:4-*dimethoxy*-8-*ethoxy*-5-*vinylphenanthrene*, $C_{20}H_{20}O_3$, which crystallises in yellow plates, m. p. 78°, and on oxidation yields 3:4-*dimethoxy*-8-*ethoxyphenanthrene*-5-*carboxylic acid*, $C_{19}H_{18}O_5$, crystallising in yellow needles, m. p. 191° (corr.); the latter substance, when heated at 195—205° under a pressure of 15 mm., yields 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*, $C_{18}H_{18}O_3$, leaflets, m. p. 100°, the *picrate* of which forms dark red needles, m. p. 119°. W. H. G.

Morphine Series. V. Synthesis of 3 : 4-Dimethoxy-8-ethoxyphenanthrene obtained by the Degradation of Thebenine. ROBERT PSCHORR and F. ZEIDLER (*Annalen*, 1910, **373**, 75—79).—An account of the synthesis of 3 : 4-dimethoxy-8-ethoxyphenanthrene, which is identical with the compound derived from ethebenine (compare preceding abstract).

o-*Ethoxybenzyl chloride*, $C_9H_{11}OCl$, is formed by the action of hydrogen chloride on *o*-ethoxybenzyl alcohol; it is an oil with an unpleasant odour, b. p. 125°/15 mm., and when boiled with potassium cyanide in acetone yields the *o-ethoxyphenylacetonitrile*, $C_{10}H_{11}ON$, a highly refractive liquid, b. p. 135—140°/16 mm.; the latter substance, when hydrolysed with alcoholic potassium hydroxide, yields *o-ethoxyphenylacetic acid*, $C_{10}H_{12}O_3$, a crystalline substance, m. p. 103°. The sodium salt of the latter substance, when heated with 2-nitro-3 : 4-dimethoxybenzaldehyde and acetic anhydride under pressure at 100° for ninety hours, yields *a-2'-ethoxyphenyl-2-nitro-3 : 4-dimethoxycinnamic acid*, $NO_2·C_6H_2(OMe)_2·CH:C(C_6H_4·OEt)·CO_2H$, which forms yellow crystals, m. p. 196°, and when reduced with ferrous sulphate and aqueous ammonia yields the corresponding *amino*-compound,

$$C_{19}H_{21}O_5N,$$

yellow prisms, m. p. 153°. The latter substance is converted through the diazo-derivative into 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*-9-*carboxylic acid*, $C_{19}H_{18}O_5$, which crystallises in glistening needles, m. p. 265°, and when heated with glacial acetic acid at 220° for eight hours yields 3 : 4-*dimethoxy*-8-*ethoxyphenanthrene*, $C_{18}H_{18}O_3$, which crystallises in leaflets, m. p. 100°, and forms a *picrate*, $C_{18}H_{18}O_3,C_6H_3O_7N_3$, red needles, m. p. 119°. W. H. G.

Morphine Series. VI. Transformation of Chloromethylmorphimethine into the Quaternary Salt of a Cyclic Base Derived from Phenanthrene. ROBERT PSCHORR and F. DICKHÄUSER (*Annalen*, 1910, **373**, 80—84).—A concentrated ethereal solution of chloromethylmorphimethine (compare Pschorr, Abstr., 1906, i, 877), when heated with alcohol at 100°, yields methylmorphol and probably chloroethyldimethylamine; instead of the latter compound, however, the polymeride, *N*-dimethylpiperazine dimethochloride, is obtained. On the other hand, chloromethylmorphimethine, when heated with benzene, yields an amorphous *substance*, which has the properties of a phenol and behaves as the salt of a quaternary base; the corresponding *methiodide* could not be obtained in a crystalline form, but when treated with aqueous sodium hydroxide and methyl sulphate, and subsequently with potassium iodide, yields a *methiodide*,

$$C_{19}H_{21}O_2N,MeI,$$

which contains two methoxy-groups, and crystallises with $1\frac{1}{2}H_2O$ in efflorescent, glistening needles. W. H. G.

Strychnos Alkaloids. VIII. Coloured Isomeric Salts of Cacothelin Base. HERMANN LEUCHS and FRIEDRICH LEUCHS (*Ber.*, 1910, **43**, 1042—1051).—Bidemethylnitrobrucine hydrate (Moufang and Tafel, Abstr., 1899, i, 309) probably has the composition represented by the formula $C_{21}H_{21}O_7N_3$. It is shown that the base gives

rise to three groups of isomeric salts. The ordinary yellow salts, of which cacothelin is the nitrate, are transformed into isomeric green salts under the influence of sulphurous acid, and the green salts in their turn are transformed into violet salts. The function of the sulphurous acid appears to be purely catalytic, and the change can take place to a certain extent in the absence of the catalyst. Stannous chloride is a more efficient catalyst than sulphurous acid, and with this reagent it is difficult to isolate the intermediate green salts. Stannic chloride, zinc chloride, zinc and hydrochloric acid, and hydrogen sulphide do not act as catalysts.

Moufang and Tafel's nitrobrucine hydrate is shown to be identical with the base of cacothelin; it does not contain methoxy-groups.

A *sulphite*, $C_{21}H_{21}O_7N_3,H_2SO_3$, has been prepared by the action of sulphurous acid on the nitrate. It forms heavy, glistening, nearly colourless prisms.

The sulphate, $C_{21}H_{21}O_7N_3,H_2SO_4$, has been isolated in the yellow, green, and violet modifications. When the solution of the violet compound is kept, it changes to brown and ultimately to pale yellow, and the addition of dilute sulphuric acid to these two solutions yields the green and yellow salts respectively.

The violet *chloride*, $C_{21}H_{21}O_7N_3,HCl,2H_2O$, forms heavy, reddish-violet, rectangular prisms, and is the stable form. The yellowish-red chloride contains $1H_2O$, and forms minute, massive prisms or three- and six-sided plates, and decomposes at 250°. The green compound is unstable, and forms short prisms.

The nitrate has also been isolated in the three forms. J. J. S.

Syntheses with the Aid of Magnesium Pyrrole Compounds. II. Alkyl Pyrryl Ketones BERNARDO ODDO (*Ber.*, 1910, 43, 1012—1021. Compare Abstr., 1909, i, 672).—Acyl chlorides react readily with magnesium pyrryl iodide, yielding ketones of the type: $NH<\begin{matrix} C(CO\cdot R):CH \\ CH=\!=\!=CH \end{matrix}$. In many cases the reaction is so violent that the addition of dry ether is necessary. The following have been synthesised by this method: 2-pyrryl methyl ketone and the corresponding ethyl, propyl, phenyl, and benzyl ketones. The yields are about 50—60% for the aliphatic, and about 80% for the aromatic, ketones. Several of these ketones have been prepared previously by Ciamician and Dennstedt (Abstr., 1885, 378), or by Dennstedt and Zimmermann (Abstr., 1887, 844), but the present method is preferable.

2-*Pyrryl propyl ketone*, $C_4NH_4\cdot CO\cdot C_3H_7$, forms colourless needles, m. p. 48·5°, b. p. 235—237°, and has an odour of butyric acid. The *phenylhydrazone*, $C_{14}H_{17}N_3$, forms pale straw-coloured needles, m. p. 80·5°. When oxidised with alkaline permanganate, the ketone yields the acid, $C_4NH_4\cdot CO\cdot CO_2H$ (compare Ciamician and Dennstedt, *loc. cit.*).

Neither oxime nor phenylhydrazone could be obtained from phenyl pyrryl ketone, which has b. p. 305—307°. Pyrryl ethyl ketone yields a *phenylhydrazone*, $C_{13}H_{15}N_3$, m. p. 111—112°, and benzyl pyrryl ketone, a *phenylhydrazone*, $C_{18}H_{17}N$, m. p. 133°.

The ketones react with magnesium methyl iodide in much the same manner as the original pyrrole. Indole also reacts with Grignard compounds. J. J. S.

Transformation of Oximinotriphenylpyrrole. FRANCESCO ANGELICO and C. LABISI (*Gazzetta*, 1910, **40**, i, 417—423).—The ordinary methods of oxidation yield unsatisfactory results with oximinotriphenylpyrrole (compare Angeli and Angelico, Abstr., 1901, i, 45; Angelico and Calvello, Abstr., 1901, i, 747), which is, however, oxidised by means either of amyl nitrite in ethereal or alcoholic solution or of potassium permanganate in acetone solution, yielding the *compound*, $\begin{matrix}\text{CPh:CPh}\\ \text{N}\!=\!\!=\!\text{CPh}\end{matrix}\!\!>\!\text{C:NO·O·NO:C}\!<\!\!\begin{matrix}\text{CPh:CPh}\\ \text{CPh:N}\end{matrix}$, as a red, crystalline powder, m. p. 190° (decomp.).

Reduction of this compound by means of zinc dust and acetic acid, hydroxylamine, ammonium sulphide, alcohol at a high temperature, or zinc dust and ammonium chloride yields the corresponding aminotriphenylpyrrole, whilst sodium arsenite or sulphide in alkaline solution gives oximinotriphenylpyrrole, which is probably a product intermediate between the new compound and aminotriphenylpyrrole. T. H. P.

New Trimethylenepyrrole Derivatives. I. MARIO GHIGLIENO (*Atti R. Accad. Sci. Torino*, 1910, **45**, 346—356).—The compound described by Guareschi and Grande (Abstr., 1900, i, 111) as 3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (dicyanohomocaronimide) is found to consist of a mixture of two apparently stereoisomeric compounds, the heterocyclic complex being, in the one case, on the side of the methyl group, and in the other, on the side of the ethyl group with respect to the trimethylene nucleus; this view is supported by the absence of such isomerism with the corresponding diethyl derivative.

α-3 : 5-Dicyano-4-methyl-4-ethyltrimethylenedicarbonimide,

$$\text{NH}\!<\!\!\begin{matrix}\text{CO·C(CN)}\\ \text{CO·C(CN)}\end{matrix}\!\!>\!\text{CMeEt},$$

forms colourless, rhombic crystals or prisms, m. p. 241—243° (decomp.) or 248—249° (Maquenne block). It has the normal molecular weight in boiling acetone, and has distinct acid properties, titration with sodium hydroxide in presence of phenolphthalein indicating it to be a monobasic acid. It is not attacked by bromine or alkaline permanganate, but by dilute sodium hydroxide (2 or 4 mols.) it is converted into the sodium salt of the monobasic acid,

$$\text{NH}\!<\!\!\begin{matrix}\text{CO·C(CO}_2\text{H)}\\ \text{CO·C(CO·NH}_2)\end{matrix}\!\!>\!\text{CMeEt},$$

or of the dibasic acid, $\text{NH}\!<\!\!\begin{matrix}\text{CO·C(CO}_2\text{H)}\\ \text{CO·C(CO}_2\text{H)}\end{matrix}\!\!>\!\text{CMeEt}$, which are to be described later.

The β-isomeride, $C_{10}H_9O_2N_3$, forms colourless needles, m. p. 202—203°, and from ether separates in large crystals,

$$3C_{10}H_9O_2N_3,2Et_2O.$$

It is slightly more soluble than the α-form, has the normal molecular weight in boiling acetone, acts as a feeble, monobasic acid, and behaves towards dilute sodium hydroxide solution in the same way as the α-modification. T. H. P.

[Preparation of Aldehyde Condensation Products.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 218616).—A discusssion on the nature of the condensation products obtained from pyridinium chlorides with primary or secondary amines, and the preparation of dyes from these compounds (compare Zincke, Abstr., 1905, i, 241, 267, 923).

The aldehydes employed had the following general formula:

$$\begin{matrix}Alk\\Ar\end{matrix}\!>\!N\cdot CH{:}CX\cdot CY{:}CZ\cdot C\!<\!\begin{matrix}O\\H\end{matrix},$$

where Ar = aryl, Alk = alkyl, X, Y, and Z = hydrogen or other substituted groups; they were combined with dihydro-α-methylindole and various primary and secondary amines.

The *aldehyde*, NMePh·CH:CH·CH:CH·CHO, m. p. 79°, is described; it forms an *oxime*, m. p. 127°, and a *phenylhydrazone*, m. p. 141°. The *aldehyde*, $CHO\cdot CH{:}CH\cdot CH{:}CH\cdot N\!<\!\begin{matrix}C_6H_4\cdot CH_2\\CH_2-CH_2\end{matrix}$, forms dark yellow prisms, m. p. 113°.

The *aldehyde*, $CHO\cdot CH{:}CH\cdot CH{:}CH\cdot N\!<\!\begin{matrix}C_6H_4\\CHMe\end{matrix}\!>\!CH_2$, forms brownish-yellow leaflets, m. p. 126·5°; its *oxime*, yellow needles, m. p. 181°.

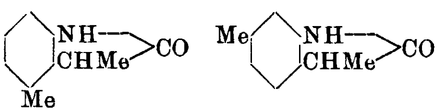
The *aldehyde*, $CHO\cdot CH{:}CH\cdot CH{:}CH\cdot N\!<\!\begin{matrix}C_6H_4-O\\CHMe\cdot CH_2\end{matrix}$, forms brown needles, m. p. 150°. F. M. G. M.

Preparation of Indoxyl and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 220172).—It is found that ethylenedianiline, $NHPh\cdot CH_2\cdot CH_2\cdot NHPh$, its homologues, or derivatives when heated at 270—290° with alkali hydroxides and alkaline earth oxides are converted into indoxyls, from which indigotin derivatives are readily obtained. The preparations of indigotin from ethylenedianiline and of methylindoxyl from ethylenedi-*o*-toluidine are described in the patent. F. M. G. M.

Preparation of Indolinones from β-Acyl-*m*-tolylhydrazide. C. F. BOEHRINGER and SÖHNE (D.R.-P. 218477 and 218727).—The formation of indolinones by heating β-acylphenylhydrazines with calcium oxide has previously been described; the reaction with *o*- or *p*-tolylacylhydrazides is found to take place readily, whilst with *m*-tolylacylhydrazides isomeric indolinones are obtained, which are of great therapeutic value.

β-Propionyl-*m*-tolylhydrazide, m. p. 31°, prepared from propionyl chloride and *m*-tolylhydrazine, is heated at 200° with calcium oxide in the presence of an indifferent gas until the evolution of nitrogen ceases;

the two isomeric *indolinones* (annexed formulæ), m. p. 110° and 148—149°, are separated by extraction with benzene and subsequent crystallisation from methyl alcohol; they are sparingly soluble in water,



readily so in mineral acids or alkalis, and reduce ammoniacal silver solutions. The second patent states that this reaction takes place at a lower temperature if sodium methoxide is employed.

F. M. G. M.

Derivatives of Tetrahydroquinoline. FRANZ KUNCKELL (*Ber. deut. Pharm. Ges.*, 1910, **20**, 183—200).—A short account has been given already of some derivatives of tetrahydroquinoline, and in the present paper further compounds are described, which are likely to be of use in characterising this base (compare Abstr., 1905, i, 297).

6-Bromotetrahydroquinoline, prepared as described already (*loc. cit.*), yields a *hydrobromide*, m. p. 193—194°, a *sulphate*, m. p. 163°, *nitrate*, m. p. 199—200°, and a *platinichloride*, m. p. 204°, all of which are crystalline. On oxidation with permanganate, it furnishes pyridine-2:3-dicarboxylic acid, indicating that the bromine atom is in the benzene ring. On treatment with sodium nitrite, it gives a *nitroso-amine*, m. p. 89—90°, which crystallises in small, colourless needles, and on reduction is converted into the corresponding hydrazine, which condenses with benzaldehyde, yielding a crystalline product. Nitrous anhydride applied by Störmer's method (Abstr., 1899, i, 42) to 6-bromo-tetrahydroquinoline yields 6-*bromo*-8-*nitrotetrahydroquinolinenitroso-amine*, m. p. 120—121°, which crystallises in brick-red needles, gives Liebermann's reaction, and when heated with acetic acid passes into 6-*bromo*-8-*nitrotetrahydroquinoline*, m. p. 131—132°, crystallising in dark red plates and possessing no basic properties. This bromo-nitro base is reduced by stannous chloride to the corresponding *amino*-derivative, m. p. 85—86°, which crystallises in colourless needles, reduces platinic chloride solution, and gives an intensely red coloration with ferric chloride in presence of hydrochloric acid. The *hydrochloride*, m. p. 184°, crystallises in colourless leaflets, and forms with stannous chloride an *additive product*, $(C_9H_{11}N_2Br,HCl)_2SnCl_2,2H_2O$, m. p. 158—160° (decomp.), which forms rosettes of colourless needles, and is the form in which the amine is first isolated after reduction (see above).

When 6-bromotetrahydroquinoline, dissolved in alcohol at 30°, is treated with nitrous anhydride, 6:8-*dinitrotetrahydroquinoline*, m. p. 165—166°, is obtained; it crystallises from acetic acid or alcohol on addition of water, and is devoid of basic properties.

Acetyltetrahydroquinoline platinichloride, m. p. 146—147°, forms small, hard, reddish-brown crystals. On bromination the acetyl base yields either 6-bromoacetyltetrahydroquinoline hydrobromide (Abstr., 1905, i, 297) or *tribromotetrahydroquinoline hydrobromide*, depending on the conditions observed. The second of these has m. p. 252—253°, and forms a green, crystalline powder, which on addition of water

passes into a yellow *substance*, m. p. 169—171°, which crystallises from alcohol in small, colourless needles.

6-*Bromo*-8-*nitroacetyltetrahydroquinoline*, m. p. 155°, obtained by nitrating 6-bromoacetyltetrahydroquinoline, forms yellow leaflets, and is not basic. On reduction with stannous chloride, it yields a stannous chloride *additive product* with the hydrochloride of the corresponding amino-derivative, $(C_9H_{10}BrN_2Ac,HCl)_2SnCl_2$, m. p. over 270°, which crystallises in colourless or faintly yellow crusts. T. A. H.

Preparation of Mononitroanthraquinonylquinolines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 218476).—By the treatment of the three isomeric 1 : 2-, 2 : 1-, and 2 : 3-anthraquinonylquinolines with nitrating agents, compounds are formed which contain a nitro-group in the anthraquinone nucleus.

Nitroanthraquinonyl-1 : 2-*quinoline*, m. p. 248°, is a grey powder insoluble in water and alkalis, and soluble in mineral acids with yellow coloration.

Nitroanthraquinonyl-2 : 1-*quinoline*, yellow needles, m. p. 258°, is more readily soluble than the 1 : 2-isomeride.

Nitroanthraquinonyl-2 : 3-*quinoline*, yellowish-white crystals, m. p. 305°, is very sparingly soluble. F. M. G. M.

Naphthindole Bases. JOSEF ZANGERLE (*Monatsh.*, 1910, **31**, 123—134).—Phenylhydrazones of aldehydes and ketones containing the *iso*propyl group, when acted on by zinc chloride in alcoholic solution, lose ammonia and form indole bases (compare Brunner, Abstr., 1896, i, 169, 625; 1900, i, 360). This reaction is now extended to α- and β-naphthylhydrazones.

Methyl iso*propyl ketone*-α-*naphthylhydrazone* is a deep red, thick fluid oil. It is converted by alcoholic zinc chloride into 3 : 3 *dimethyl*-2-*methylene*-α-*naphthindoline*, $C_{10}H_6<\begin{matrix}NH\cdot C{:}CH_2\\ \quad\ \ |\\ \quad CMe_2\end{matrix}$, which crystallises from ether; m. p. 70—71°. The *picrate* forms dark yellow crystals, m. p. 149—150°; the *stannichloride* is reddish-yellow; the *mercurichloride* crystallises in colourless needles.

1 : 3 : 3-*Trimethyl*-2-*methylene*-α-*naphthindoline*, $C_{10}H_6<\begin{matrix}NMe\cdot C{:}CH_2\\ \qquad\ |\\ \qquad CMe_2\end{matrix}$, was obtained by decomposition of the *iodide* (m. p. 229°) with potassium hydroxide as a dark blue oil. The *picrate* forms light yellow crystals, m. p. 177°, and a crystalline *ferrichloride* and *platinichloride* were obtained.

1 : 1-Dimethyl-2-methylene-β-naphthindoline (or 3 : 3-dimethyl-2-methylene-ββ-naphthindoline) is best prepared by the action of alcoholic oxalic acid on the β-naphthylhydrazone of methyl *iso*propyl ketone. It has m. p. 115°, and is identical with the base described by Fischer and Steche (Abstr., 1887, 588). The iodide has m. p. 224—225°, the picrate also m. p. 224—225°, the acetate has m. p. 109°, and the benzoate forms colourless, flat crystals, m. p. 114°. Treatment with methyl iodide yields the tertiary base mixed with secondary base, which latter was removed as nitrosoamine, reddish-yellow crystals, m. p. 175—176°.

1 : 1 : 3-*Trimethyl-2-methylene-β-naphthindoline* (or 1 : 3 : 3-*trimethyl-2-methylene-ββ-naphthindoline*) has m. p. 119—120°; it turns blue on exposure to the atmosphere. The *iodide* crystallises in minute, colourless needles, m. p. 233°. E. F. A.

Preparation of Transformation Products of Ketens and Carbimides. GEORG SCHROETER (D.R.-P. 220852).—The greater part of the work described in this patent has been previously recorded (compare Abstr., 1909, i, 617, 773).

The following new compounds are mentioned: *Phenyltetrahydroxazolone*, m. p. 87—88·5°, obtained from phenylhydracrylic acid hydrazide. *Piperonyltetrahydroxazolone*, m. p. 122—123°, prepared from *piperonylhydracrylic acid hydrazide*, m. p. 173—174·5°. The methylation of piperonyltetrahydroxazolone yields *piperonylmethyltetrahydrooxazolone*, m. p. 108—109°, which on treatment with cold concentrated hydrochloric acid is converted into *methyleneadrenaline*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NHMe.$$

F. M. G. M.

Synthesis of Oxazoles and Thiazoles. II. SIEGMUND GABRIEL (*Ber.*, 1910, **43**, 1283—1287).—It is shown that the reaction between compounds of the type of ω-benzoylaminoacetophenone and phosphorus pentachloride or pentasulphide (this vol., i, 190) is a fairly general one, and proceeds in the same manner when either or both the phenyl groups in ω-benzoylaminoacetophenone are replaced by aliphatic groups.

ω-Acetylaminoacetophenone, $NHAc{\cdot}CH_2{\cdot}COPh$, obtained by acetylating ω-aminoacetophenone hydrochloride with acetic anhydride and sodium acetate, crystallises in long, flat needles, m. p. 85·5—86·5°. The *hydrochloride* crystallises in flat, pointed needles, which lose hydrogen chloride on exposure to the air; the *platinichloride* crystallises in glistening rhombohedra, decomposing at 166°; the *aurichloride*, $2C_{10}H_{11}ON,HAuCl_4$, decomposes at 125°, and the *chromate*,

$$2C_{10}H_{11}ON,H_2CrO_4,$$

forms orange-red, rhombic plates, m. p. 83°, after sintering at 78°.

The crude acetyl derivative reacts with phosphorus pentachloride, yielding *5-phenyl-2-methyloxazole*, $O{<}\begin{matrix}CMe{:}N\\ CPh{:}CH\end{matrix}$, which crystallises in glistening plates, m. p. 58—59°, b. p. 255·5°/748 mm. The oxazole yields a *chromate*, which crystallises in rhombic plates. *5-Phenyl-2-methylthiazole*, $S{<}\begin{matrix}CMe{:}N\\ CPh{:}CH\end{matrix}$, obtained by heating the acetyl derivative with twice its weight of phosphorus pentasulphide for ten minutes at 170°, is pale yellow in colour, and has m. p. 81°. The *hydrochloride* crystallises in long needles; the *aurichloride* is precipitated as an oil which solidifies to yellow needles; the *platinichloride*, $2C_{10}H_9NS,H_2PtCl_6$, is sparingly soluble, and decomposes at 210°; the *chromate* forms orange-yellow needles, m. p. 108° (decomp.), and the *picrate*, flat prisms, m. p. 255—256°.

Benzoylaminoacetone, $COPh{\cdot}NH{\cdot}CH_2{\cdot}COMe$, obtained by benzoylating aminoacetone hydrochloride (Gabriel and Colman, Abstr., 1903,

i, 13), crystallises in needles, m. p. 85° (decomp.), and reacts with phosphorus pentachloride, yielding *2-phenyl-5-methyloxazole*,

$$O<\begin{matrix}CPh\colon N\\ \vert\\ CMe\colon CH\end{matrix},$$

as an oil, b. p. 254—255°/734 mm. The *hydrochloride*, $C_{10}H_9ON,HCl$, forms glistening prisms and plates; the *aurichloride*, lemon-yellow needles; the *platinichloride*, striated prisms, which decompose at 218°, and the *chromate*, orange-yellow needles.

2-Phenyl-5-methylthiazole, $S<\begin{matrix}CPh\colon N\\ CMe\colon CH\end{matrix}$, has b. p. 283·5°/750 mm., and has an odour of quinoline. The chromate and aurichloride are sparingly soluble, and the *platinichloride*, $2C_{10}H_9NS,H_2PtCl_6$, crystallises in yellow, rhombic plates, which decompose at 245°.

Crude acetylaminoacetone reacts with phosphorus pentachloride, yielding *2 : 5-dimethyloxazole*, $O<\begin{matrix}CMe\colon N\\ CMe\colon CH\end{matrix}$, with b. p. 117—118°/755 mm. It has an odour of pyridine, and yields a crystalline picrate, aurichloride, and platinichloride. The same acetyl derivative reacts with phosphorus pentasulphide, yielding 2 : 5-dimethylthiazole (Hubacher, Abstr., 1891, 222). J. J. S.

Mutual Replacement of Semicarbazone and Phenylhydrazone. GUSTAV KNÖPFER (*Monatsh.*, 1910, **31**, 87—110. Compare Abstr., 1909, i, 188).—Phenylhydrazine and semicarbazide radicles mutually replace one another. The reaction is reversible and not complete; an equilibrium is reached, depending on the relative quantities of the interacting substances, which is not influenced by temperature. At least 5 mols. of the decomposing reagent are required to make the interchange practically complete. To test the relative strength of the attachment of the two groups, the action of aldehydes and ketones was studied towards a molecular mixture of phenylhydrazine and semicarbazide, but, as a rule, mixtures of both compounds were obtained, and no regularity could be detected. Differences in solubility also appear to have no great influence, although the semicarbazones are sparingly soluble and the hydrazones easily soluble.

Azines may be converted into hydrazones (Abstr., 1909, i, 188), but the reverse change could not be effected. The hydrazones of a large number of aldehydes and ketones were dissolved in alcohol, and set aside with three times the theoretical quantity of hydrazine sulphate and sodium carbonate. Only in the case of resorcylaldehyde was the azine formed.

The conversion of semicarbazone into hydrazone was effected in alcoholic or acetic acid solution; the reverse change was carried out by dissolving the phenylhydrazone in alcohol and adding semicarbazide, hydrochloride, and potassium acetate, dissolved in a minimum of water.

Derivatives of the following were investigated: benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, vanillin, anisaldehyde, cuminaldehyde, piperonal, furfuraldehyde, *o*-, *m*-, and *p*-nitrobenzaldehydes,

cinnamaldehyde, dimethylaminobenzaldehyde, resorcylaldehyde, protocatechualdehyde, acetophenone, *p*-aminoacetophenone, ω-bromo- and ω-chloro-acetophenones, and styryl methyl ketone.

Furfuraldehydesemicarbazone crystallises in brownish-yellow needles, m. p. 202—203°, but does not react with phenylhydrazine, nor does the reverse change take place. *Dimethylaminobenzaldehydesemicarbazone* forms colourless needles, decomp. 221—222°. *Resorcylaldehydesemicarbazone* separates in bright yellow crystals, which become red at 210°, decomp. 260°. *Protocatechualdehydesemicarbazone* is similar, and decomposes at 230°.

p-*Aminoacetophenonesemicarbazone* forms yellow crystals, m. p. 250° (decomp.); the *phenylhydrazone* forms faint yellow crystals, m. p. 110—114°; its *hydrochloride* is colourless (decomp. 215°), and not red, m. p. 207°, as described by Münchmeyer (Abstr., 1887, 482), and it does not react with semicarbazide. ω-*Bromoacetophenonesemicarbazone* separates in colourless crystals, m. p. 146°; only resinous substances were obtained from it on treatment with phenylhydrazine. ω-*Bromoacetophenonesemicarbazone* exhibits similar behaviour towards phenylhydrazine; it forms colourless, sparingly soluble crystals, m. p. 156°. Phenylhydrazine reacts with the ketone to form the same yellow halogen-free compound, m. p. 137°, as obtained by Hess (Abstr., 1886, 547) and Culmann (Abstr., 1890, 1268) from the bromo-compound.

E. F. A.

Synthesis with Diazomethane. New Preparation of Pyrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1910, 40, i, 117—120).—β-Methyl-Δ^{β}-butylene and stilbene do not react with diazomethane, the substitution of several aliphatic or aromatic radicles for the ethylene hydrogen atoms apparently preventing the reaction.

The presence of one phenyl group, as in styrene, is also unfavourable to the reaction with diazomethane, which takes place slowly, giving 4-*phenylpyrazoline*, $NH<\begin{matrix}CH_2\cdot CHPh\\ N{=\!=}CH\end{matrix}$, which was analysed in the form of the *platinichloride*, $(C_9H_{10}N_2)_2,H_2PtCl_6$, and, on oxidation with bromine water, is converted into 4-phenylpyrazole (compare Buchner and Dessauer, Abstr., 1893, i, 282).

The interaction of vinyl bromide and diazomethane yields pyrazole hydrobromide; the unstable 5-bromopyrazoline, $NH<\begin{matrix}CHBr\cdot CH_2\\ N{=\!=\!=}CH\end{matrix}$, is doubtless formed first, and is transformed into pyrazole by loss of hydrogen bromide, since Curtius and Wirsing (Abstr., 1895, i, 248) found that attempts to brominate pyrazoline always result in the formation of pyrazole. The readiness with which vinyl bromide and diazomethane react, confirms the view that the synthesis is favoured by the presence of a negative substituent group in the ethylene derivative.

T. H. P.

Preparation of Aqueous Soluble Compounds from 1-Phenyl-2:3-dimethyl-5-pyrazolones and Mono- or Di-alkylglycollic Acids of Formulæ $C_5H_{10}O_3$ and Upwards. J. D. RIEDEL (D.R.-P. 218478).—Soluble compounds from 1-phenyl-2:3-dimethyl-5-pyrazolone

(antipyrine) with alkylglycollic acids are readily prepared by melting together molecular proportions of the two components either with or without a diluent.

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*iso*butyrate*,

$$OH\cdot CMe_2\cdot CO_2H,C_{11}H_{12}ON_2,$$

colourless, prismatic needles, m. p. 71—72·5°, is prepared from dimethylglycollic acid (α-hydroxy*iso*butyric acid).

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-α-*ethylbutyrate*, m. p. 77·5—78·5°, crystallises from water.

1-*Phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-α-*methylbutyrate*,

$$CMeEt(OH)\cdot CO_2H,C_{11}H_{12}ON_2,$$

m. p. 64—65·5°, is prepared in ethereal solution.

The hydrolysis of methyl *iso*propylketocyanohydrin,

$$CHMe_2\cdot CMe(OH)\cdot CN,$$

yields α-hydroxy-αβ-dimethylbutyric acid, m. p. 72—72·5°, which combines with antipyrine to form 1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* α-*hydroxy*-αβ-*dimethylbutyrate*, $CHMe_2\cdot CMe(OH)\cdot CO_2H,C_{11}H_{12}ON_2$, m. p. 78—79·5°.

Antipyrine α-*hydroxy*iso*valerate*, $CHMe_2\cdot CH(OH)\cdot CO_2H,C_{11}H_{12}ON_2$, forms prisms, m. p. 62—63°. The aqueous solutions of these substances give a bluish-red coloration with ferric chloride, and with sodium nitrite the green colour characteristic of oximino-antipyrines.

F. M. G. M.

Derivatives of Acetyltetronic Acid. ERICH BENARY (*Ber.*, 1910, **43**, 1065—1069. Compare Abstr., 1909, i, 890).—α-Acetyltetronic acid forms a phenylhydrazone, an oxime, a semicarbazone, and a hydrazone. It is the carbonyl group of the acetyl group which reacts, as the same phenylhydrazone is formed when the amide,

$$O{<}\begin{array}{l}CO-C{:}CMe\cdot NH_2\\ CH_2\cdot CO\end{array},$$

reacts with an alcoholic solution of phenylhydrazine. The above-mentioned derivatives possess acidic properties.

α-*Acetyltetronic acid phenylhydrazone*, $O{<}\begin{array}{l}CO-CH\cdot CMe{:}N_2HPh\\ CH_2\cdot CO\end{array}$, separates from methyl alcohol in rhombic crystals, m. p. 162—163° (decomp.), and when boiled with acetyl chloride and dry ether yields unaltered hydrazone, together with 1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazole*-4-*carboxylolactone*, $O{<}\begin{array}{l}CO-C\cdot CMe\\ CH_2\cdot C\cdot NPh\end{array}{>}N$, which crystallises in colourless needles, m. p. 151—152°. The pyrazole derivative can also be obtained by boiling the hydrazone with amyl alcohol and phenylhydrazine hydrochloride. When boiled with methyl-alcoholic potassium hydroxide, the lactone yields 1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazole*-4-*carboxylic acid*, $OH\cdot CH_2\cdot C{<}\begin{array}{l}NPh——N\\ C(CO_2H)\cdot CMe\end{array}$, which crystallises in slender needles, decomposing at 212°. The potassium salt, when oxidised with permanganate, yields 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid.

When heated at 250°, the acid loses carbon dioxide, and yields

1-*phenyl*-3-*methyl*-5-*hydroxymethylpyrazolone*, $OH\cdot CH_2\cdot C\!\!<\!\!\begin{matrix} NPh\cdot N \\ CH-CMe \end{matrix}$, which crystallises in small plates, m. p. 116—117°.

a-Acetyltetronic acid semicarbazone, $C_7H_9O_4N_3$, crystallises in soft, felted needles, m. p. 212—213° (decomp.). The *oxime*, $C_6H_7O_4N,H_2O$, forms colourless needles, and when anhydrous melts at 149—150°.

The *hydrazone*, $C_6H_8O_3N_2$, forms colourless needles, m. p. 186—187°, and yields a *benzylidene* derivative, $C_{13}H_{12}O_3N_2$, m. p. 212—213°.

The *ketazine*, $C_{12}H_{12}O_6N_2$, crystallises in yellowish-green needles, which decompose at 225°. J. J. S.

Dehydracetic Acid. ERICH BENARY (*Ber.*, 1910, **43**, 1070—1075. Compare Perkin, Trans., 1887, **51**, 494; Stollé, Abstr., 1905, i, 838; Bülow, *ibid.*, 1909, i, 95).—Stollé's product, $\begin{matrix} O-CO-C-CMe \\ CMe{:}CH\cdot C\cdot NPh \end{matrix}\!\!>\!\!N$, melting at 158°, when boiled with alcoholic potassium hydroxide and acidified yields 1-*phenyl*-3-*methyl*-5-*acetonylpyrazole*-4-*carboxylic acid*, $CH_2Ac\cdot C\!\!<\!\!\begin{matrix} C(CO_2H)\cdot CMe \\ NPh-\!\!-\!\!-N \end{matrix}$, which crystallises in small needles, m. p. 178—179°, and yields a sparingly soluble, crystalline *silver* salt, $C_{14}H_{13}O_3N_2Ag$. When heated for a short time at 220—230°, the acid loses water and yields the original compound, m. p. 158°. The *methyl* ester of the acid, $C_{15}H_{16}O_3N_2$, crystallises in colourless needles, m. p. 125°; the *oxime*, $C_{14}H_{15}O_3N_3$, has m. p. 209—211°. When oxidised, the acid yields 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid, m. p. 202—203° (Bülow and Schlesinger, Abstr., 1900, i, 56).

A much better yield (60%) of Stollé's lactone is formed when a methyl-alcoholic solution of dehydracetic acid is boiled with phenylhydrazine hydrochloride. It is accompanied by a *product*, $C_{13}H_{12}N_2$, m. p. 195—196°, which is not decomposed when boiled with alcoholic potassium hydroxide, and can be separated by this means from the lactone.

The behaviour of dehydracetic acid towards phenylhydrazine is analogous to that of acetyltartronic acid, and thus favours Feist's formula. J. J. S.

So-called Unsymmetric Methyl Azinsuccinate. AUGUST DARAPSKY (*Ber.*, 1910, **43**, 1095—1111).—On heating ethyl diazosuccinamate with or without pyridine, a colourless, crystalline compound, m. p. 209°, is obtained, which gives a characteristic reaction with nitrous acid. It has the composition $C_{10}H_{12}O_5N_4$, and is derived from two molecules of the ester with elimination of a molecule of nitrogen and a molecule of alcohol.

This reaction is similar to the condensation of methyl diazosuccinate to *as*-methyl azinsuccinate (Curtius and Koch, Abstr., 1885, 886), m. p. 154°. This condensation product is now shown, however, to be identical with methyl 3 : 4 : 5-tricarboxypyrazolineacetate, obtained by Buchner and Witter (Abstr., 1894, i, 346) by the condensation of methyl aconitate and methyl diazoacetate.

Presumably, methyl diazosuccinate, $CO_2Me\cdot CH_2\cdot CN_2\cdot CO_2Me$, is

converted into methyl fumarate, $CO_2Me\cdot CH{:}CH\cdot CO_2Me$, which condenses with a second molecule of diazosuccinate to the pyrazoline,
$NH\!<\!\begin{array}{l}N\!=\!=\!=\!=\!=\!=\!=\!=\!=\!=\!=\!=\!=\!=\!C\cdot CO_2Me\\ C(CO_2Me)(CH_2\cdot CO_2Me)\cdot CH\cdot CO_2Me\end{array}$. In confirmation of this, the condensation product is obtained in increased yield by the condensation of methyl fumarate and methyl diazosuccinate.

This synthesis proves the acetic acid residue to occupy position 5. By these operations, as Buchner and Witter (*loc. cit.*) found, a stereoisomeric ester, m. p. 104°, is obtained in small quantity.

In a similar manner, ethyl diazosuccinamate is, in part, converted into ethyl fumaramate, $CO_2Et\cdot CH{:}CH\cdot CO\cdot NH_2$, which condenses with ethyl diazosuccinamate to form an amic acid ester,

$$NH\!<\!\begin{array}{l}C(CO\cdot NH_2)(CH_2\cdot CO_2Et)\cdot CH\cdot CO_2Et\\ \text{———————————}N{:}C\cdot CO\cdot NH_2\end{array}.$$

Alcohol is eliminated from this, forming *ethyl* 3 : 4 : 5-*tricarboxypyrazoline*-5-*acetate-amide-imide*,

$$\begin{array}{l}CO\cdot CH_2\\ NH\cdot CO\end{array}\!>\!C\!<\!\begin{array}{l}NH\text{———}N\\ CH(CO_2Et)\end{array}\!>\!C\cdot CO\cdot NH_2.$$

With nitrous acid the oximino-derivative is obtained. Proof of this structure is afforded by hydrolysis with sodium hydroxide to the corresponding acid, and methylation by means of diazomethane to the above-described methyl ester, m. p. 154°.

Ethyl diazosuccinamate is prepared by diazotising ethyl aspartate; attempts to obtain it by the action of ammonia on ethyl diazosuccinate led to a very violent explosion.

Ethyl 3 : 4 : 5-*tricarboxypyrazoline*-5-*acetate-amide-imide* forms colourless, intergrown, lustrous plates, m. p. 209° (decomp.), or when quickly heated, m. p. 215°. The *oximino*-derivative forms bright yellow, glistening plates, m. p. 198° (decomp.); it is soluble in alkali hydroxides with a yellowish-red coloration.

Methyl 3 : 4 : 5-tricarboxypyrazoline-5-acetate, obtained either from the above ethyl ester amide-imide or from methyl diazoacetate and trimethyl aconitate, or from dimethyl diazosuccinate and dimethyl fumarate, crystallises in colourless bunches of needles, m. p. 154°; at the same time a more soluble isomeride, m. p. 104°, is obtained, which is converted by hydrogen bromide in acetic acid into the higher melting ester. Nitrous acid is without action. E. F. A.

So-called Symmetrical Methylazinsuccinate. AUGUST DARAPSKY (*Ber.*, 1910, 43, 1112—1126).—Both methyl and ethyl azinsuccinate were obtained as oils by Curtius (Abstr., 1885, 886) by coupling four molecules of diazoacetic ester. Buchner (Abstr., 1901, i, 232) suggested that in reality these oils represented impure esters of pyrazolinetricarboxylic acid. This supposition is now confirmed; the methylazin ester gives a series of liquid fractions of high boiling point containing nitrogen, and further purification of one of these yielded methyl *cyclo*propanetricarboxylate. The oil obtained on prolonged heating of ethyl diazoacetate at 120—130° gave, when kept, crystals of ethyl pyrazolinetricarboxylate. On distillation of the oil, *ethyl* trans-cyclo*propane*-1 : 2 : 3-*tricarboxylate*

was obtained, and identified by comparison with a synthetical product. It is a thick, colourless oil, b. p. 159—160°/9 mm.

Ethyl diazoacetate condenses both at 100° and at 120°; probably ethyl fumarate is first formed from two molecules. This condenses with a further molecule of ethyl diazoacetate to ethyl pyrazoline-3:4:5-tricarboxylate, $NH<\begin{matrix} N{=\!=\!=\!=\!=}C\cdot CO_2Et \\ CH(CO_2Et)\cdot CH\cdot CO_2Et \end{matrix}$. E. F. A.

4:6-Dimethyl-2-pyrimidone. III. Condensation with Aromatic Aldehydes. OTTO STARK and MAX BÖGEMANN (*Ber.*, 1910, **43**, 1126—1131. Compare Abstr., 1909, i, 260).—The authors have condensed 4:6-dimethyl-2-pyrimidone with vanillin, protocatechualdehyde, and *p*-dimethylaminobenzaldehyde by the method previously described. In these cases only one methyl group reacts, so that only derivatives of the monobenzylidene type are obtained. With regard to the colour of the substances obtained from vanillin and protocatechualdehyde, the theory previously put forward holds good, but the dimethylaminobenzylidene derivative forms two series of differently-coloured salts. Phosphoric acid and all organic acids in all concentrations yield violet salts containing one molecule of acid. Very dilute (*N*/10) mineral acids (except nitric acid) also yield violet salts of the same type, but if the concentration of the acid exceeds *N*/3, yellow salts containing two molecules of acid are formed. Nitric acid yields yellow solutions at all concentrations. The yellow solutions become violet on dilution. It is suggested that the violet salts have the constitution:

$$NH<\begin{matrix} CO-NH \\ CMe{:}CH \end{matrix}>C{:}CH\cdot CH{:}C_6H_4{:}NMe_2Cl,$$

whilst to the yellow salts the formula

$$N\lessgtr\begin{matrix} CO\cdot N(HCl) \\ CMe-CH_2 \end{matrix}>C\cdot CH{:}CH\cdot C_6H_4\cdot NMe_2,HCl$$

is ascribed.

4-p-*Hydroxy*-m-*methoxybenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{14}H_{14}O_3N_2$ (from vanillin), crystallises in yellow needles, m. p. 254°. The *hydrochloride* forms reddish-brown needles, m. p. 250° (sintering at 240°). The substance also yields a reddish-brown *acetate*, and a *sulphate* of the same colour, whilst the *nitrate* is yellowish-brown. The acetic acid solution dyes raw silk and cotton brown, but the colour is not fast to alkali.

4-m-p-*Dihydroxybenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{13}H_{12}O_3N_2$ (from protocatechualdehyde), could not be obtained in good crystalline form. On heating to 300°, it loses colour, but does not melt. It dissolves in *N*/2-acids only on warming; in the case of nitric acid, this heating destroys the substance. The *sulphate*, *hydrochloride*, and *acetate* are brown. An acetic acid solution of the substance dyes raw silk, wool, and cotton brown, but the colour is not fast to alkali.

4-p-*Dimethylaminobenzylidenemethyl*-6-*methyl*-2-*pyrimidone*, $C_{15}H_{17}ON_3$,

crystallises in small, red laminæ, m. p. 250—252° (sintering at 245°). The *dihydrochloride* is prepared in alcoholic solution with hydrogen chloride in the absence of moisture, and crystallises in yellow needles. It rapidly turns violet in the air. The *monohydrochloride* is obtained by allowing the dihydrochloride to remain in a vacuum over potassium hydroxide. Acetic acid solutions of the substance dye silk, wool, and cotton violet, but the colour is not fast to alkali. R. V. S.

Preparation of Leuco-derivatives of Indigotins. EMANUEL MERCK and WILHELM FLIMM (D.R.-P. 217945).—When the products obtained by the condensation of grape or starch sugar with aromatic *o*-aminocarboxylic acids are fused with potassium hydroxide, and the dark or orange-red fusion subjected to atmospheric oxidation, derivatives of indigotin are obtained.

Glucoseanilide-o-carboxylic acid,

$$CO_2H\cdot C_6H_4\cdot N\colon CH\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH,$$

m. p. 126—128°, is prepared by heating an alcoholic solution of anthranilic acid with dextrose; on fusion with alkaline hydroxide, followed by oxidation, indigotin is produced. F. M. G. M.

Action of Primary Amines on Indigotin. EUGÈNE GRANDMOUGIN (*Ber.*, 1910, **43**, 1317—1318).—It is pointed out that the quindoline derivative obtained from aniline and indigotin (Abstr., 1909, i, 968) does not appear to be identical with Knecht's product (*J. Soc. Dyers*, 1898, **14**, 163). J. J. S.

Preparation of Bromoindigotin Sulphide. LEOPOLD CASSELLA & Co. (D.R.-P. 220321, 220629).—By the action of sulphur chloride (SCl_2) and sulphur bromide on indigotin at a temperature of about 160°, substituted indigotin sulphides are obtained.

Dibromoindigotin sulphide, $C_{16}H_6O_2N_2Br_2S$, is a blue powder, insoluble in most organic solvents, except nitrobenzene, and forms a valuable vat dye.

The second patent indicates that the preparation of brominated indigotin sulphides takes place readily when indigotin, bromine, and sulphur are heated together at a temperature above 160° in a diluting agent such as nitrobenzene or chlorobenzene.

Tribromoindigotin sulphide, prepared in this manner, is a dark blue, insoluble powder. F. M. G. M.

3-Aminotetrahydroquinazoline-2:4-dione or 3-Aminobenzoylenecarbamide. FRANZ KUNCKELL (*Ber.*, 1910, **43**, 1021—1024. Compare Abstr., 1905, i, 382).—*3-Aminotetrahydroquinazoline-2:4-dione*, $C_6H_4<\begin{matrix}CO-N\cdot NH_2\\ NH\cdot CO\end{matrix}$, obtained by heating tetrahydroquinazoline-2:4-dione with hydrazine hydrate solution at 160—180° during twelve hours, crystallises in colourless needles, m. p. 290—291°. It sublimes readily, and reduces Fehling's solution and ammoniacal solutions of silver and platinum salts. When heated with concentrated hydrochloric acid at 160—170°, it is not decomposed, but when heated with 20% sodium hydroxide solution the amino-group is removed. The *hydrochloride*, $C_8H_7O_2N_3,HCl$, forms colourless needles, and decom-

poses at 289°. The *sulphate*, $2C_8H_7O_2N_3,H_2SO_4$, has m. p. 259—260°. The *acetyl* derivative, $C_6H_4<\begin{matrix}CO-N\cdot NHAc\\ NH\cdot CO\end{matrix}$, forms small, glistening needles, m. p. 250°, and the *di cetyl* derivative, $C_{12}H_{11}O_4N_3$, glistening needles, m. p. 212°.

3-Methylaminotetrahydroquinazoline-2 : 4-dione,

$$C_6H_4<\begin{matrix}CO-N\cdot NHMe\\ NH\cdot CO\end{matrix},$$

obtained by methylating the amino-compound, forms small needles, m. p. 263°. *3-Benzylideneaminotetrahydroquinazoline-2 : 4-dione,*

$$C_6H_4<\begin{matrix}CO-N\cdot N\colon CHPh\\ NH\cdot CO\end{matrix},$$

has m. p. 240°. The *potassium* salt, $C_6H_4<\begin{matrix}CO-N\cdot NH_2\\ NK\cdot CO\end{matrix},EtOH$, forms colourless prisms, and loses the alcohol of crystallisation at 180°.

J. J. S.

Constitution of 3-Aminotetrahydroquinazoline-2 : 4-dione and Some of its Derivatives. FRANZ KUNCKELL (*Ber.*, 1910, **43**, 1234—1238).—Proof is given in two ways that by the action of hydrazine hydrate on tetrahydroquinazoline-2 : 4-dione the imino-group in position 3 is replaced by the group $N\colon\cdot NH_2$ (compare preceding abstract).

In the first place, 1-methyltetrahydroquinazoline-2 : 4-dione was heated with hydrazine hydrate in a sealed tube at 160° to form *3-amino-1-methyltetrahydroquinazoline-2 : 4-dione,*

$$C_6H_4<\begin{matrix}CO-N\cdot NH_2\\ NMe-CO\end{matrix}.$$

This crystallises in colourless needles, m. p. 165°, and is identical with the substance prepared by the action of methyl iodide on the potassium salt of 3-aminotetrahydroquinazolinedione.

The *benzylideneamino*-compound forms colourless needles, m. p 157°; the o-*hydroxybenzylideneamino*-derivative, prepared by interaction with salicylaldehyde, m. p. 160°, crystallises in lustrous, colourless plates; the *acetylamino*-derivative separates in colourless needles, m. p. 140°; the *methylamino*-derivative likewise crystallises in needles, m. p. 153°.

Secondly, 3-phenyltetrahydroquinazoline-2 : 4-dione,

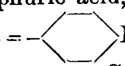
$$C_6H_4<\begin{matrix}CO-NPh\\ NH-CO\end{matrix},$$

prepared by heating anthranilic acid and monophenylcarbamide at 180°, reacts with hydrazine, forming aniline and the 3-aminotetrahydroquinazoline-2 : 4-dione already described (*loc. cit.*). In addition, *o*-aminobenzhydrazide, m. p. 120—122°, and a substance crystallising in needles, m. p. 208—209°, are formed.

E. F. A.

Combination of Triphenylmethane Dyes with the Indigotin Group. FRITZ REITZENSTEIN and WILHELM BREUNING (*Annalen*, 1910, **372**, 257—286).—A continuation of the investigation on the effect of an accumulation of a large number of chromophoric groups on

the colour of a compound (compare Reitzenstein and Rothschild, Abstr., 1906, i, 316; Reitzenstein and Schwerdt, Abstr., 1907, i, 648). The compounds dealt with in this paper differ from those described in the previous communications in that the long carbon chain is replaced by the indigotin residue: $\begin{array}{l}-CO\\-NH\end{array}\!\!>C{:}C<\!\!\begin{array}{l}CO-\\NH-\end{array}$.

Isatin, *o*-methylisatin, and *p*-methylisatin condense with tetramethyldiaminobenzhydrol under the influence of concentrated sulphuric acid, yielding the substances (I), (II), and (III) respectively [R = –NMe_2].

$$\text{(I.)}\quad CO<\begin{array}{l}CO-C{:}CH\cdot C\cdot CHR_2\\NH\cdot C{:}CH\cdot CH\end{array}\qquad \text{(II.)}\quad CO<\begin{array}{l}CO-C{:}CH-C\cdot CHR_2\\NH\cdot C{:}CMe\cdot CH\end{array}$$

$$\text{(III.)}\quad CO<\begin{array}{l}CO-C{:}C(CHR_2)\cdot CMe\\NH\cdot C{:}CH\text{——}CH\end{array}\quad\text{or}\quad CO<\begin{array}{l}CO-C{:}CH\cdot CMe\\NH\cdot C{:}CH\cdot C\cdot CHR\end{array}$$

These compounds are converted by phosphorus pentachloride into the corresponding substituted isatin chlorides, which, when treated with glacial acetic acid and zinc dust, yield the related di-indoxyl compound; for example, the substance (I) yields ditetramethyldiaminodiphenylmethyldi-indoxyl (IV).

The di-indoxyl derivatives, although leucoindigotin compounds, are not oxidised by atmospheric oxygen; indeed, the properties of the indigotin grouping are almost entirely obliterated by the presence of the triphenylmethyl complexes.

5-(4′:4″)-Tetramethyldiaminodiphenylmethylisatin (I) condenses with dimethylaniline in the presence of zinc chloride, yielding 5-(4′:4″)-tetramethyldiaminodiphenylmethyl-3:3-bis-*p*-dimethylaminophenyloxindole (V), which when oxidised by lead dioxide in acetic acid is converted into 4-amino-1:3-*bis*di-*p*-dimethylaminophenylmethylbenzene (VI) (compare Baeyer and Lazarus, Abstr., 1886, 155; Liebermann and Danaïla, Abstr., 1907, i, 976).

$$\text{(IV.)}\quad \left[\begin{array}{l}C(CHR_2)\cdot CH{:}C\cdot C(OH)\\CH\text{——}CH\text{——}C\text{——}NH\end{array}\!\!>C-\right]_2\qquad \text{(V.)}\quad \begin{array}{l}C(C_6H_4\cdot NMe_2)_2\cdot CO\\C_6H_3(CHR_2)\text{——}NH\end{array}$$

$$\text{(VI.)}\quad CH<\begin{array}{l}C(NH_2){:}C[CH(C_6H_4\cdot NMe_2)_2]\\CH\text{——}C[CH(C_6H_4\cdot NMe_2)_2]\end{array}\!\!>CH.$$

A comparison of the dyes described in this paper shows that the colour depends largely on the absence or presence of methyl groups, and on their positions relatively to the fundamental carbon atom; compounds without a methyl group attached directly to the benzene nucleus are blue or bluish-violet, those with a methyl group in the ortho-position are green, whilst others with a methyl group in the meta-position are blue with a decided red tint. The colour is rendered more intense by the introduction of the –NH·CO·CO– group with the –NH– in the para-position, but not in the meta-position; in all cases, however, the colours are more brilliant and of a purer shade. Contrary to the general rule, the effect of increasing the size of the molecule, as in the case of the di-indoxyl derivatives, is not always to produce a change of colour towards violet.

5-(4′:4″)-*Tetramethyldiaminodiphenylmethylisatin* (I) is a yellowish-brown powder, and when oxidised by lead dioxide yields the corre-

sponding dye, which dyes wool a pure blue; the *acetyl* derivative, $C_{27}H_{27}O_3N_3$, is a bluish-white powder, and does not melt at 335°; the corresponding *chloride*, $CHR_2 \cdot C_6H_3 < \begin{matrix} CO \\ N \end{matrix} > CCl$, is a green powder, which when treated with glacial acetic acid and zinc dust yields *ditetramethyldiaminodiphenylmethyldi-indoxyl* (IV), a yellowish-brown powder which begins to decompose at 160°; the oxidised leuco-base dyes wool an intense deep blue.

5-(4′ : 4″)-*Tetramethyldiaminodiphenylmethyl*-7-*methylisatin* (II) is a yellowish-brown powder, m. p. 200—202°; after oxidation it dyes wool an intense blue with a reddish-tint. *Ditetramethyldiaminodiphenylmethyldi*-o-*methylindoxyl*, $C_{52}H_{56}O_2N_6$, is a bluish powder; it commences to decompose at 200° and sinters at 223°; when oxidised with lead dioxide, it dyes wool a brilliant violet.

4(or 6)-4′ : 4″-*Tetramethyldiaminodiphenylmethyl*-5-*methylisatin* (III) is a reddish-brown powder, m. p. 261°; the *sodium* salt is orange and has m. p. 222°. *Ditetramethyldiaminodiphenylmethyldi*-p-*methylindoxyl*, $C_{52}H_{56}O_2N_6$, is a green powder, which commences to decompose at 210° and sinters at 230°; the oxidised compound dyes wool a dark grass-green.

5-(4′ : 4″)-*Tetramethyldiaminodiphenylmethyl*-3 : 3-bis-p-*dimethylaminophenyloxindole* (V) is a yellowish-red, crystalline powder; it commences to decompose at 100°, and sinters at 120°. 4-*Amino*-1 : 3-bis*di*-p-*dimethylaminophenylmethylbenzene* (VI) is a white, crystalline powder, m. p. 149—150°; when oxidised with lead dioxide, it yields an intense blue solution with a faint red tint. W. H. G.

Syntheses with Diazomethane. II. E. OLIVERI-MANDALÀ (*Gazzetta*, 1910, **40**, i, 120—124).—Peratoner and Azzarello (Abstr., 1907, i, 979) and Peratoner and Palazzo (Abstr., 1907, i, 1018) found that the methyl or phenyl radicle in aceto- or benzo-nitrile hinders condensation with diazomethane, whilst the strongly negative halogen or cyanogen radicles have a favourable influence.

The author finds that condensation with diazomethane or diazoethane is facilitated by the carboxymethyl group of methyl cyanoformate. In this case the action proceeds in two stages:

$$(1)\ CO_2Me \cdot CN + NH < \begin{matrix} CH \\ \| \\ N \end{matrix} = NH < \begin{matrix} N{:}C \cdot CO_2Me \\ | \\ N{:}CH \end{matrix},$$

and (2) the latter $+ NH < \begin{matrix} CH \\ \| \\ N \end{matrix} = NMe < \begin{matrix} N{:}C \cdot CO_2Me \\ | \\ N{:}CH \end{matrix}$. Both these products were isolated, the 2-methyl-1 : 2 : 3-triazole-4-carboxylic acid being identical with that obtained by Peratoner and Azzarello (*loc. cit.*) by hydrolysing 4-cyano-2-methyl-1 : 2 : 3-triazole.

The action of diazoethane on methyl cyanoformate yields the methyl ester of 4-*methyl*-2-*ethyl*-1 : 2 : 3-*triazole*-5-*carboxylic acid*,

$$NEt < \begin{matrix} N{:}C \cdot CO_2H \\ | \\ N{:}CMe \end{matrix};$$

the free acid forms shining, feathery scales, m. p. 131°. T. H. P

Diazo-derivatives of [1 : 2 : 4-]Triazole. WILHELM MANCHOT (*Ber.* 1910, **43**, 1312—1317).—*Phenyldiazotriazole hydrate*, $C_8H_7ON_5$, obtained by treating phenylaminotriazole with an excess of nitrous acid, forms a yellow, crystalline precipitate, and, like the diazotriazolecarboxylic acid and its ester, is comparatively stable (compare Thiele and Manchot, Abstr., 1899, i, 168; Manchot and Noll, Abstr., 1906, i, 213). It is quite harmless when moist, but in the dry state explodes when heated, rubbed or struck, and liberates iodine from an acidified solution of potassium iodide. The compound can be used for the preparation of other derivatives of phenyltriazole; when the moist diazo-compound is added carefully to hydrobromic acid (D = 1·7°) at 0°, 5-*bromo*-3-*phenyl*-1 : 2 : 4-*triazole*, $CBr\begin{matrix}\diagup NH\cdot N \\ \diagdown N \text{---} CPh\end{matrix}$, is obtained as compact prisms, m. p. 186—188°, which can be reduced with water and sodium amalgam to 3-phenyltriazole, m. p. 116° (Young, Trans., 1905, **87**, 626, gives 119—120°).

When reduced with stannous chloride and hydrochloric acid, the diazo-compound yields *phenyl*-1 : 2 : 4-*triazylhydrazine*, which forms a crystalline hydrochloride, $C_8H_9N_5,2HCl$, m. p. 198°, after sintering at 150°. The hydrazine reacts with aldehydes and ketones in alcoholic solutions, yielding hydrazones. The *benzylidene* derivative, $C_{15}H_{13}N_5$, forms prismatic crystals, m. p. 233°; the *anisylidene* compound, $C_{16}H_{15}ON_5$, has m. p. 195°; the o-*hydroxybenzylidene* derivative, $C_{15}H_{13}ON_5$, forms long needles, m. p. 269°, and the α-*phenylethylidene* derivative, $C_{16}H_{15}N_5$, long prisms, m. p. 255°.

Several condensation products of aminotriazoles and aldehydes have been prepared. *Piperonylideneamino*-3-*phenyl*-1 : 2 : 4-*triazole*, $C_{16}H_{20}O_2N_4$, forms slender needles, m. p. 194°, and *piperonylideneaminomethyltriazole*, $C_{11}H_{10}O_2N_4$, small prisms, m. p. 207°. J. J. S.

Action of Ammonia on ω-Nitrobenzaldehyde-*p*-nitrophenylhydrazone. GIACOMO PONZIO (*Gazzetta*, 1910, **40**, i, 77—86).—By the action of sodium methoxide, ω-nitrobenzaldehyde-*p*-nitrophenylhydrazone is converted into α-dinitrotetraphenyltetrazoline (compare Bamberger and Grob, Abstr., 1901, i, 296), and a similar transformation is effected by the action of alcoholic potassium hydroxide (compare this vol., i, 192). With alcoholic ammonia, however, this compound yields (1) a small proportion of α-dinitrotetraphenyltetrazoline, and 2) a compound, $C_{13}H_{12}O_2N_4$, which is formed in 75—80% yield; the fact that this compound forms stable salts and gives a triazole when treated with acetic anhydride, together with the simultaneous formation of α-dinitrotetraphenyltetrazoline, indicates that the amino-group present occupies the position of the ω-nitro-group, so that it represents ω-aminobenzaldehyde-*p*-nitrophenylhydrazone (benzenyl-*p*-nitrophenylhydrazidine), $HN_2\cdot CPh:N\cdot NH\cdot C_6H_4\cdot NO_2$. This reaction, if of general application, affords a simple means of preparing substituted hydrazidines.

ω-*Aminobenzaldehyde*-p-*nitrophenylhydrazone*, $C_{13}H_{12}O_2N_4$, forms green prisms with a red reflexion, or reddish-brown needles with a

green reflexion, m. p. 150—151°, and has strongly basic properties, dissolving readily in all acids, and giving faintly yellow solutions; in alkali hydroxide solutions it dissolves, with formation of an intense wine-red coloration, but decomposes gradually with evolution of ammonia. Its *hydrochloride*, $C_{13}H_{12}O_2N_4,HCl$, forms yellow prisms, m. p. 245° (decomp.), and its *oxalate*, $C_{13}H_{12}O_2N_4,H_2C_2O_4$, faintly straw-yellow plates, m. p. 212° (decomp.).

3-*Phenyl*-1-p-*nitrophenyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_4\cdot N<\begin{matrix}N{=\!=}CPh\\ CMe{:}N\end{matrix},$$

prepared by the action of acetic anhydride on ω-aminobenzaldehyde-*p*-nitrophenylhydrazone, forms faintly yellow, rhombic plates, m. p. 142°. T. H. P.

New Method of Preparation of Hydrazidines. GIACOMO PONZIO (*Gazzetta*, 1910, 40, i, 312—324).—By the method already described (see preceding abstract), the author has prepared a number of hydrazidines (amidrazones), which are all stable, intensely coloured compounds, forming hydrochlorides and, when they contain a *p*-nitro-substituent, oxalates. By the action of acetic anhydride they are converted into complex triazoles: $NH_2\cdot CR{:}N\cdot NH\cdot ArNO_2 \longrightarrow NHAc\cdot CR{:}N\cdot NH\cdot ArNO_2 \longrightarrow \begin{matrix}N{:}CMe\\ CR{=}N\end{matrix}>N\cdot ArNO_2$, which are not obtainable otherwise.

ω-*Nitrobenzaldehyde*-o-*nitrophenylhydrazone*,

$$NO_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

obtained in theoretical yield by the interaction of *o*-nitrobenzene-diazonium sulphate and the sodium salt of ω-nitrotoluene, forms orange-red needles, m. p. 138—147°.

ω-*Aminobenzaldehyde*-o-*nitrophenylhydrazone*,

$$NH_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

prepared by the action of alcoholic ammonia on the preceding compound, forms brown prisms with green reflexion, m. p. 178°, and its *hydrochloride*, $C_{13}H_{12}O_2N_4,HCl$, shining, yellow plates, m. p. 258° (decomp.).

3-*Phenyl*-1-o-*nitrophenyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_4\cdot N<\begin{matrix}N{=\!=}CPh\\ CMe{:}N\end{matrix},$$

obtained by the action of acetic anhydride on ω-aminobenzaldehyde-*o*-nitrophenylhydrazone, forms faintly yellow needles, m. p. 143—144°.

ω-*Aminobenzaldehyde*-p-*nitro*-o-*tolylhydrazone*,

$$NH_2\cdot CPh{:}N\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

obtained by the action of alcoholic ammonia on ω-nitrobenzaldehyde-*p*-nitro-*o*-tolylhydrazone (compare Abstr., 1909, i, 443; this vol., i, 192), crystallises in bronze-coloured plates with green reflexion, m. p. 119° (decomp.); its *hydrochloride*, $C_{14}H_{14}O_2N_4,HCl$, in yellow plates, m. p. 280° (decomp.), and its *oxalate*, $C_{14}H_{14}O_2N_4,H_2C_2O_4$, in yellow prisms, m. p. 232° (decomp.). With acetic anhydride, it yields 3-*phenyl*-1-p-*nitro*-o-*tolyl*-5-*methyl*-1 : 2 : 4-*triazole*,

$$NO_2\cdot C_6H_3Me\cdot C_2N_3PhMe,$$

which crystallises in straw-coloured, four-sided plates, m. p. 163—164°.

ω-Aminobenzaldehyde-o-*nitro*-p-*tolylhydrazone*,

$$NH_2\cdot CPh\colon N\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

prepared from the corresponding ω-nitro-derivative, forms slender, reddish-brown needles with green reflexion, m. p. 149°, and its *hydrochloride*, $C_{14}H_{14}O_2N_4,HCl$, yellow prisms, m. p. 260° (decomp.). Acetic anhydride, converts it into 3-*phenyl*-1-o-*nitro*-p-*tolyl*-5-*methyl*-1 : 2 : 4-*triazole*, $NO_2\cdot C_6H_3Me\cdot C_2N_3PhMe$, which crystallises in slightly yellow prisms, m. p. 120°.

ω-Aminobenzaldehyde-o-*chloro*-p-*nitrophenylhydrazone*,

$$NH_2\cdot CPh\colon N\cdot NH\cdot C_6H_3Cl\cdot NO_2,$$

crystallises in orange-red or golden-yellow needles, m. p. 167—168°; its *hydrochloride* in flattened, straw-coloured needles, m. p. 278° (decomp.), and its *oxalate* in yellow laminæ, m. p. 245° (decomp.). By acetic anhydride, it is converted into 3-*phenyl*-1-o-*chloro*-p-*nitrophenyl*-5-*methyl*-1 : 2 : 4-*triazole*, $NO_2\cdot C_6H_3Cl\cdot C_2N_3PhMe$, which crystallises in slender, straw-coloured needles, m. p. 129°. T. H. P.

Reaction of Diazoalkyls with 1-Phenyl-2-methylurazole. SIDNEY NIRDLINGER, E. K. MARSHALL, jun., and SALOMON F. ACREE (*Amer. Chem. J.*, 1910, **43**, 424—425).—A supplementary note to the previous paper (this vol., i, 341). Experiments are being made on the action of diazoalkyls on 1-phenyl-2-methylurazole at 0° and −70°. The ratios of the *N*- and *O*-esters obtained by the action of methyl iodide on the silver salt of 1-phenyl-2-methylurazole in 40% alcohol are the same whether the silver salt is suspended or dissolved. The ratios of the *N*- and *O*-esters obtained when the sodium, zinc, and silver salts of the urazole in alcohol-ether solution at −70° are treated with hydrochloric acid in presence of diazomethane are almost the same in each case, namely, 87 : 13. The urazole itself in alcohol-ether solution at 20°, 0°, or −70° gives a ratio 94 : 6, and hence it is evident that the salts have approximately the same equilibrium constants, and that these are slightly different from those for the urazole. The cause of this difference is being investigated. E. G.

Preparation of Substituted Halogen Iminodialkylpyrimidines. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 217946).—When iminodialkylpyrimidines are treated with halogenating agents, two atoms of halogen combine with the iminic nitrogen. 4-*Dichloroamino* 5 : 5-*diethylpyrimidine*-2 : 6-*dione*, $\begin{matrix} NH\cdot CO\cdot C(Et)_2 \\ | \qquad\quad | \\ CO\text{-}N{=}C\cdot NCl_2 \end{matrix}$, m. p. 147°, is thus prepared from 4-imino-5 : 5-diethylpyrimidine-2 : 6-dione. Prolonged boiling with water converts these substances into dialkylbarbituric acids. F. M. G. M.

Diazopyrroles. FRANCESCO ANGELICO and C. LABISI (*Gazzetta*, 1910, **40**, i, 411—417).—It has been shown previously (Abstr., 1909, i, 122) that the cinnabar-red isomeride, into which diazotriphenylpyrrole is converted by prolonged boiling with dilute sulphuric acid, is oxidised by nitric acid to a diketone, the latter being transformed by zinc and acetic acid into the furan derivative corresponding with the diazo-

triphenylpyrrole. The authors now find that the reverse transformation of the furan derivative into diazotriphenylpyrrole can be effected by heating the former compound with alcoholic ammonia or ammonium acetate in a sealed tube.

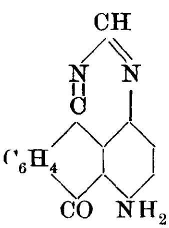
The action of alcoholic ammonium sulphide solution on the diketone, m. p. 163°, yields: (1) the *compound*, $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}N{=\!=\!=\!=}N} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}C(SPh){=}C{\cdot}SPh\ (?)}\end{array}$, which forms yellow scales, m. p. 206—207° (slight decomp.), and yields a green substance on reduction with zinc dust and acetic acid; the fact that this green substance sublimes and gives a dark green solution with sulphuric acid indicates that it is probably formed by the elimination of one of the original sulphur atoms, the second of these taking part in the formation of a thiophen nucleus; (2) a small quantity of a faintly yellow *compound*, m. p. 196—197°.

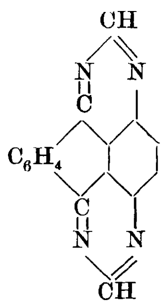
The following salts of diazotriphenylpyrrole were prepared and analysed: the *sulphate*, $C_{22}H_{15}N_3,H_2SO_4$, greenish-yellow needles, m. p. 190° (decomp.); the *picrate*, $C_{22}H_{15}N_3,C_6H_3O_7N_3$, brown needles, m. p. 206° (decomp.), and the *nitrate*, $C_{22}H_{15}N_3,HNO_3$, m. p. 175° (decomp.), which is accompanied by a small proportion of an intensely yellow, crystalline compound, m. p. 183°.

The action of magnesium ethyl iodide on diazotriphenylpyrrole yields an intensely yellow compound, $C_{24}H_{21}N_3$, m. p. 120°.

T. H. P.

Preparation of Anthrapyrimidines and of Anthrapyrimidones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 220314).—4-*Amino*-1-*anthrapyrimidine* (I) is formed by the condensation of 1 : 4-diaminoanthraquinone with one molecular proportion of formamide; with two molecules of formamide, *anthradipyrimidine* (II) is produced. 1-*Anthrapyrimidone*, yellow prisms, is prepared by heating together α-aminoanthraquinone, carbamide, and phenol.


(I.)


(II.)

The condensation of 4-amino-1-methylaminoanthraquinone with β-chloroanthraquinone yields 1-*methylamino*-4-β-*anthraquinonyl*-*aminoanthraquinone*, a dark blue powder, which when heated with carbamide, zinc chloride, and phenol forms 4-β-*anthraquinonylamino*-1-N-*methylanthrapyrimidone*.

4-p-*Tolylamino*-1-*anthrapyrimidone*, bronze prisms, is prepared from 1-amino-4-*p*-tolylaminoanthraquinone. The tinctorial properties of these compounds are described in the patent. F. M. G. M.

Chloroanthranilic Esters and their Condensation with Nitrosobenzene. PAUL FREUNDLER (*Compt. rend.*, 1910, **150**, 1179—1181).—Directions are given for the preparation of *o*-carboxylic azo-compounds by direct chlorination of methyl anthranilate

and condensation of the product with nitrosobenzene (compare Abstr., 1906, i, 158). Condensation of methyl 5-chloroanthranilate with nitrosobenzene at the ordinary temperature gives, in addition to the *o*-azo-ester, azoxybenzene and a yellow *compound*,

$$C_{14}H_{11}O_3N_2Cl,$$

m. p. 137°. The reaction is represented as $3C_6H_5\cdot NO + C_8H_8O_2NCl = C_{14}H_{11}O_3N_2Cl + ON_2Ph_2 + H_2O$, and the constitution of the new compound as

$$CO_2Me\cdot C_6H_2Cl\genfrac{<}{>}{0pt}{}{NH}{O}NPh \text{ or } CO_2Me\cdot C_6H_2Cl\genfrac{<}{}{0pt}{}{N\cdot NHPh}{O}.$$

The substance is feebly basic, and forms blood-red, crystalline salts with mineral acids; the *acetyl* derivative crystallises in bronze-like needles, m. p. 124—125°. Hydrolysis with alkaline sodium hydroxide leads to the formation of a brownish-yellow *acid*, which, on reduction with zinc dust and subsequent oxidation in the air, furnishes a red *acid*. The latter forms a red *benzoyl* derivative, $C_{14}H_{10}O_3N_2ClBz$, m. p. 166°.

Analogous products were not obtained from methyl 3 : 5-dichloro- or 3 : 5-dibromo-anthranilate. W. O. W.

Diazohydrazo-compounds (Tetrazens). Diazo-compounds from Aminoguanidine. KARL A. HOFMANN, HEINRICH HOCK, and RUDOLF ROTH (*Ber.*, 1910, **43**, 1087—1095. Compare this vol., i, 232).—The compound obtained by the action of sodium nitrite on aminoguanidine dinitrate, and previously described (this vol., i, 232) as aminoguanidine diazohydroxide, is more probably a pseudo-base, in which one nitrogen chain contains either the nitrosoamine group, $\cdot NH\cdot NH\cdot NO$, or the *anti*-diazohydroxide group, $\cdot NH\cdot N:N\cdot OH$, it being not possible at present to decide between these alternatives. The two carbon atoms are united by the diazohydrazo-group,

$$\cdot N:N\cdot NH\cdot NH,$$

and the compound is *guanylnitrosoaminoguanyltetrazen* or *guanyldiazoguanyltetrazen*, $NH:C(NH_2)\cdot NH\cdot NH\cdot N:N\cdot C(:NH)\cdot N_3H_2O$.

By the action of sodium hydroxide, cyanamide and ammonia are formed on the one hand, and, after acidifying, tetrazylazoimide on the other. This is analogous to the decomposition of hippurylphenylbuzylene studied by Curtius (Abstr., 1893, i, 463).

Guanyldiazoguanyltetrazen is stable towards ammonia, and neutral to litmus. It gives a reddish-yellow coloration with β-naphthol in alcoholic solution, and brownish-red and reddish-yellow colorations with α- and β-naphthylamine.

To exclude the possibility of the diazohydroxide containing a closed tetrazole ring, *guanyltetrazyltetrazen*,

$$NH:C(NH_2)\cdot NH\cdot NH\cdot N:N\cdot CN_4H,$$

was prepared by the interaction of diazotetrazole and aminoguanidine in acetic acid solution, and obtained as a bright yellow powder (compare Thiele, Abstr., 1892, 1295).

This is far less explosive than the diazohydroxide, is more soluble, and is acid towards litmus. It dissolves without colour in ethereal perchloric acid solution, and immediately reacts with silver nitrate, forming a yellow explosive silver salt. Decomposition by sodium

hydroxide likewise yields cyanamide, ammonia, and tetrazylazoimide.

When the diazohydroxide is decomposed by sodium hydroxide, the *compound*, $N_3{\cdot}C(NH){\cdot}N_3H_2O$, is probably formed, which is converted into tetrazylazoimide on acidifying. The addition of copper acetate to the alkaline solution gives a dark olive-brown precipitate, from which the *copper salt*, $N_3C{<}\begin{matrix}N{-}Cu{\cdot}O \\ NH{\cdot}N{:}N\end{matrix}$, was obtained in thin, bright blue plates; this is exceedingly explosive.

Guanylazoimide perchlorate, $NH{:}C(N_3){\cdot}NH_2,HClO_4$, is obtained by the interaction of aminoguanidine dinitrate and sodium nitrite in presence of perchloric acid. It forms colourless, lustrous, doubly refractive, six-sided, thick plates. It is highly explosive, but otherwise resembles the analogous nitrate obtained by Thiele (Abstr., 1892, 1295). E. F. A.

The Quantity of Mono-amino-acids Yielded by Proteins when Hydrolysed with Acids. THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1910, **26**, 212—228).—Modifications are proposed, and full details given of them, in the methods of esterifying organic acids on the lines of Phelps and Tillotson's work. The yield so obtained of most of the mono-amino-acids from protein (zein) is then greater. W. D. H.

Partial Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1910, **65**, 417—419).—The obtaining of *d*-alanylglycine from the partial hydrolysis of silk has been repeated, and in favourable cases as much as 8% is yielded. The mode of separation and identification of this dipeptide is described. W. D. H.

Partial Hydrolysis of Proteins by Sulphuric Acid ZDENKO H. SKRAUP and E. KRAUSE (*Monatsh.*, 1910, **31**, 143—148).—Proteins are dissolved by 60% sulphuric acid to a very different extent. Twenty grams were shaken at the ordinary temperature with 200 c.c. of acid (58·5%); gelatin, silk gum, and silk fibrin are dissolved almost immediately, casein requires somewhat longer, whilst egg-albumin and edestin are not completely dissolved after thirty-six hours.

From time to time, to test the extent of hydrolysis, samples were taken, diluted with water, made just alkaline with strong ammonia, and then faintly acid with sulphuric acid, and the amount of precipitation compared. Egg-albumin and edestin give a considerable proportion of albumoses, the silk proteins very little. In the latter case, hydrolysis takes place very rapidly, but the former substances are only slowly acted on. After three-quarters of an hour's interaction in the case of silk gum, the albumose precipitate only amounts to 29%. The albumoses from casein and edestin were dried, again dissolved in sulphuric acid, and precipitated after forty hours; a considerable proportion underwent further hydrolysis. E. F. A.

Production of Putrefaction Bases. ALEXANDER ELLINGER (*Zeitsch. physiol. Chem.*, 1910, **65**, 394—396).—A reply to Ackermann

(Abstr., 1909, i, 619, and this vol., i, 288). The author's previous results (Abstr., 1900, i, 143) are confirmed. J. J. S.

Preparation and Physico-chemical Properties of Demineralised Gelatin. CHARLES DHÉRÉ and M. GORGOLEWSKI (*Compt. rend.*, 1910, **150**, 934—936).—Details are given for the preparation of ash-free gelatin by prolonged dialysis of aqueous solutions, conductivity water being employed in the last stages of the process. A more rapid method, applicable to small quantities of material, involves repeated freezing and filtration of 0·5% solutions. Whichever method is adopted, the last traces of electrolytes are removed by allowing a 2·25% solution to solidify in a U-tube, each limb of which is filled up with conductivity water; a current of 6 volts per cm. is then passed between platinum electrodes.

Gelatin prepared in this way was found to be electronegative, and to have a conductivity of $k = 5{\cdot}2 \times 10^{-6}$ in a 0·726% solution. Solutions have the power of spontaneous coagulation, although in a less degree than when electrolytes are present. A 2% solution shows a marked opalescence, which is diminished by alkalis and to a less extent by acids and salts. A 10% solution is not opalescent. W. O. W.

Pepsinglutinpeptone. MAX SIEGFRIED and H. SCHMITZ (*Zeitsch. physiol. Chem.*, 1910, **65**, 295—317).—The authors have continued the examination of this substance, which was obtained by Scheermesser (Abstr., 1904, i, 463), with a view to ascertaining whether it had a constant composition and determining its decomposition products. They have found that different preparations of the compound have the same elementary composition (C 47·65%, H 6·69%, and N 17·30%). Different preparations of the barium salt had Ba 9·74—10·19%. The rotatory power was also practically constant, varying in different cases from $[\alpha]_D^{20}$ $-81{\cdot}28°$ to $-82{\cdot}15°$. The substance when subjected to a fractional modification of the carbamino-reaction (Abstr., 1906, i, 144) yielded six fractions of barium salt, which had the same percentage of barium and the same rotatory power. Preparations of the peptone of different origins all showed the same value ($\frac{1}{7}$) for the quotient CO_2/N (compare Abstr., 1908, i, 379). β-Naphthalenesulphonyl chloride and 4-nitrotoluene-2-sulphonyl chloride yield *compounds* of constant composition, in which two of the acyl residues are present for every seven nitrogen atoms. The former has m. p. 205—210°; the latter, m. p. 165—170°. From all this the authors consider the chemical individuality and purity of the peptone to be established.

The hydrolysis of the substance was effected by means of sulphuric acid. Arginine and lysine were precipitated by addition of phosphotungstic acid, the amounts found being respectively 19·7% and 9·1%, on the assumption that no other compounds are contained in the precipitate. Glycine (49·2%), glutamic acid (9·3%), leucine, and proline were also found to be present. In the necessary separations the carbamino-reaction was largely employed. The percentages given above are the percentages of nitrogen contained in the various fractions expressed in terms of the total nitrogen of the peptone, but the amino-acids were actually isolated as well. R. V. S.

Pepsin. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1910, **45**, 224—230).—The author has prepared an exceptionally active and pure specimen of pepsin, 0·00005 gram, dissolved in 50 c.c. of 0·25% hydrochloric acid solution, being capable of dissolving 1 gram of coagulated egg-albumin in eight hours. The pepsin contained 12·09% of nitrogen, 16·30% of which was basic nitrogen, existing as ammonia, 3·39%, histidine 4·46%, arginine 4·00%, and lysine 4·43%. Of the remaining 83·70% of nitrogen, 0·98% was insoluble, whilst 7·45% was precipitated by barium hydroxide, 13·44% by barium hydroxide, and magnesium oxide, 6·57% by silver sulphate, and 4·24% by phosphotungstic acid. There is hence a marked difference between pepsin and the proteins, since in the latter the proportions of nitrogen occurring in the form of the three hexone bases vary considerably, whilst in the case of pepsin these proportions are very nearly equal. Tyrosine, leucine, and, perhaps, aspartic and glutamic acids were also obtained on hydrolysis of the pepsin. T. H. P.

Proteolytic Ferments. K. HIRAYAMA (*Zeitsch. physiol. Chem.*, 1910, **65**, 290—292).—From experiments on the action of commercial preparations of pepsin and of the gastric juice of the dog, the author has obtained results confirming the indications of Takemura (*ibid.*, **63**, 201) that these products contain another ferment of the type of β-protease. The method adopted was to act on egg-albumin with Grübler or Merck pepsin, or with the gastric juice in the presence of small quantities of acids of different strengths. The rate of solution of the protein (measured by Mett's method) and the rate of production of carboxyl groups (measured by Sörensen's formaldehyde titration) are differently affected by the change in the degree of acidity of the medium, indicating that two distinct fermentative processes are involved. R. V. S.

Influence of Reaction of the Medium on the Formation of Melanins by Diastatic Oxidation. H. AGULHON (*Compt. rend.*, 1910, **150**, 1066—1068. Compare Abstr., 1909, i, 621).—Strong acids diminish the yield of melanins obtained by the oxidation of tyrosine with an extract of *Russula queleti*, whilst boric acid and salts, such as monosodium phosphate, which are neutral to methyl-orange are without action. Salts neutral to phenolphthalein and alkaline to methyl-orange favour the formation of insoluble oxidation products, the optimum concentration being between $N/200$ and $N/100$. Sodium hydroxide and salts, such as disodium phosphate, which are alkaline to phenolphthalein favour oxidation up to an optimum concentration of $N/500$, above which they have an inhibiting effect. W. O. W.

The Influence of Neutral Salts on Ferment Action. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, **24**, 210—218).—The diastatic enzyme loses its power after dialysis. This power can, however, be restored on the addition of sodium chloride. A certain definite quantity of salt is necessary to produce the optimum action; excess above this quantity causes inhibition; the absolute and not the relative quantity is the factor determining this optimum. If a diastase solution, inactivated by dialysis, is shaken with insoluble starch, it is adsorbed. On addition of salt to a suspension of the

starch with the adsorbed ferment, the latter is reactivated. The author draws the conclusion that the adsorption is a physical and not a chemical process, as he shows that the ferment is adsorbed from a solution containing soluble starch by insoluble starch. S. B. S.

Viscosaccharase, an Enzyme which Produces Slime from Cane-Sugar. MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch., Amsterdam*, 1910, **12**, 635—649).—Certain bacteria, such as *B. mesentericus vulgatus* and *B. megatherium*, when grown on a medium of the composition: tap-water, 2% agar, 2% saccharose, 0·02% potassium nitrate, 0·02% dipotassium hydrogen phosphate, produce an emulsion. This phenomenon is due to an enzyme, *viscosaccharase*, which diffuses out into the agar-plate, and which can be precipitated (along with other enzymes) from filtered cultures of *B. mesentericus*. A reducing sugar is formed at the same time as the colloidal substance, to the formation of which the emulsion is due. The viscosaccharase appears to be an enzyme capable of producing synthesis, and a relationship is supposed to exist between the synthetically produced colloid and "dextran." Saccharose may be replaced by raffinose, but other sugars investigated do not give rise to the emulsion. S. B. S.

Enzymic Condensation of Sugars. ENRICO PANTANELLI and G. FAURE (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 389—394).—When *Aspergillus oryzae* is grown on a solid or liquid nutrient medium containing starch, its amylolytic activity increases, even after the formation of spores, and passes through a maximum after thirty to forty days at 25°. An enzyme which has the power of condensing dextrose or invert sugar first appears after thirty-five to forty days, when the amylolytic activity has begun to decline, and increases in amount slowly, but irregularly, until the eighth month, subsequently disappearing. Amylase, maltase, and invertase are found in small quantities in year-old cultures. The activity of the condensing enzyme excreted in the culture liquid is considerably less than that of the enzyme contained in the mycelium, and the authors have investigated the action of 5 c.c. of mycelium extract (1 : 5), in presence of toluene, on 15 c.c. of (1) concentrated solutions of dextrose and invert sugar (about 4 mols.) and sucrose (about 2 mols.), and (2) saturated lactose solution at 45° and at the ordinary temperature.

In a control solution of dextrose, the amount of reducing sugar per 1 c.c. diminished in one hundred and fifteen days from 0·736 to 0·528 gram, the latter figure being obtained in presence of the enzyme in four to eleven days. Cryoscopic measurements indicate, in the concentrated dextrose solutions containing enzyme, a diminution of the molecular concentration (4·09 to 3·24 mols. at 45°), so that a proportion of the original hexose molecules have undergone condensation to larger molecules possessing little or no reducing power. In the control solution of dextrose, the molecular concentration diminishes, under similar conditions, from 4·09 to 3·49, so that, in absence of enzyme, a reducing polysaccharide, probably maltose or *iso*maltose, is formed. In invert-sugar solutions, the enzyme causes loss of reducing power without effecting condensation of the sugar molecules, the reversion being hence only apparent.

Reversion of a hydrolytic change only occurs when the concentration of the products of hydrolysis exceeds that which represents equilibrium with the hydrolyst. In highly concentrated solution, the hydrolytic reaction must be regarded as bimolecular, the small proportion of water assuming the role of an active mass, and not that of a mere solvent. When, however, 2 of the 4 mols. of dextrose were replaced by 2 mols. of a neutral salt, no condensation was effected by the enzyme, the reversionary activity of which may be paralysed by the salt or its ions. If, instead of 2 mols. of neutral salt, 2 mols of mannitol were employed, condensation occurred to the extent of 36·2% at the ordinary temperature, so that either the mannitol condenses with the dextrose, or the assumption that the water figures as an active mass in the reaction is justified.

In neutral solution, the mycelium of *Aspergillus oryzae*, or its aqueous or glycerol extract, causes no condensation of maltose, but in presence of a small proportion of sodium hydroxide, condensation occurs in a syrup containing 68—70%, or even in a solution containing only 8—10% of the sugar; the synthesising enzyme which effects this condensation of maltose differs from the amylase (or dextrinase), which, in an acid medium, hydrolyses starch (or dextrin) to maltose. T. H. P.

Action of Hypophosphorous Acid on Triphenylcarbinol and on Michler's Hydrol. II. Robert Fosse (*Bull. Soc. chim.*, 1910, [iv], 7, 231—235. Compare this vol., i, 292).—When triphenylcarbinol is heated with hypophosphorous acid and the yellow product boiled with sodium hydroxide solution, an oily residue is formed, consisting of triphenylmethane with a little triphenylcarbinol; the solution yields crystals of *triphenylmethylphosphinous acid*,

$$CPh_3{\cdot}PHO{\cdot}OH,$$

m. p. 94°. When the reaction is carried out with sodium hypophosphite in presence of acetic acid and sulphuric acid, the carbinol is almost completely converted into the acid, whilst in presence of acetic acid alone, an almost quantitative yield of the hydrocarbon is obtained.

Tetramethyldiaminobenzhydrylphosphinous acid,

$$CH(C_6H_4{\cdot}NMe_2)_2{\cdot}PHO{\cdot}OH,$$

prepared from Michler's hydrol, occurs in colourless crystals, m. p. 90°. This acid reduces an alcoholic solution of silver nitrate on boiling. W. O. W.

Reduction Products of Arsanilic Acid and its Derivatives. I. *p*-Aminophenylarsinic Oxide. Paul Ehrlich and Alfred Bertheim [and, in part, E. Schmitz] (*Ber.*, 1910, 43, 917—927).—Arsanilic acid may be reduced to *p*-aminophenylarsenic oxide (1) with sulphurous acid in presence of hydrogen iodide as catalyst, or (2) with phenylhydrazine, or (3) with phosphorus trichloride, in an indifferent diluent, such as ethyl acetate. The last method is the least satisfactory in the particular case studied.

p-minophenylarsenic oxide, $NH_2{\cdot}C_6H_4{\cdot}AsO,2H_2O$, softens at 80°, becomes liquid, and decomposes at 100°. The anhydrous substance softens at 90°, partly melts at 100°, becomes solid, and melts to a

clear and transparent liquid at 185—186°. It has only very faint acid properties, but is a strong reducing agent. It forms azo-dyes of yellow colour with a distinct red tinge, and a red *condensation product* with β-naphthaquinonesulphonic acid, very sparingly soluble in sodium carbonate.

In the amino-compound the bond between arsenic and carbon is much looser than in arsanilic acid; in addition, it behaves as an unsaturated compound, the arsenic tending to react as a quinquevalent atom. Accordingly, it is very reactive.

Hydrogen chloride converts it into *triaminotriphenylarsine*,

$$As(C_6H_4\cdot NH_2)_3;$$

this forms glistening, four-cornered plates, m. p. 173—174°; the *triacetate* crystallises in colourless needles, which soften at 170°, m. p. 232—233°. Iodine oxidises it to *triacetaminotriphenylarsenic oxide*, $AsO(C_6H_4\cdot NHAc)_3$.

p-Aminophenylarsenic oxide reacts with chloroacetic acid, forming p-*aminophenylarsinoacetic acid*, $NH_2\cdot C_6H_4\cdot AsO(OH)\cdot CH_2\cdot CO_2H$, crystallising in plates, m. p. 162° (decomp.).

The halogen alkyls react similarly. E. F. A.

Preparation of Arsenoaryl-glycollic and -thioglycollic Acids. [Arsenoaryl-oxy- or -thio-acetic Acids.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 216270. Compare Abstr., 1909, i, 279, 280, 348).—The reduction of hydroxyarylarsinic acids has been described previously, but it is now found that with such strong reducing agents as sodium amalgam or sodium hyposulphite, products of the following general formula are produced:

$$2CO_2H\cdot CH_2\cdot R\cdot A\cdot AsO(OH)_2 + 8H = CO_2H\cdot CH_2\cdot R\cdot A\cdot As\colon As\cdot A\cdot R\cdot CH_2\cdot CO_2H,$$

A = aryl; R = oxygen or sulphur.

Phenylglycol-p-*arsinic acid*, prepared by heating sodium *p*-hydroxyphenylarsinate in aqueous alkaline solution with chloroacetic acid, crystallises from water, sinters about 150°, and carbonises on further heating.

Phenylthioglycol-p-*arsinic acid*, readily soluble in hot alcohol, is produced when diazotised *p*-aminophenylarsinic acid is boiled with potassium xanthate in alkaline solution and subsequently treated with chloroacetic acid; it sinters at 170°, and decomposes about 187°.

Arsenomandelic acid, $As_2(C_6H_4\cdot O\cdot CH_2\cdot CO_2H)_2$, is obtained when sodium phenylglycol-*p*-arsinate is reduced in alkaline solution at 45° with sodium hyposulphite and magnesium chloride; the *sodium* salt is yellow, and readily soluble in water, from which the free acid separates as a voluminous precipitate on acidification; it reduces cold ammoniacal silver nitrate.

Arsenophenylthiolacetic acid has similar properties; it is prepared by heating phenylthioglycol-*p*-arsinic acid with phenylhydrazine in methyl alcoholic solution, when *arsenoxidephenylthiolacetic acid* is formed; sodium amalgam is then added, when *sodium arsenophenylthiolacetate* separates as a yellow precipitate.

These compounds have powerful trypanocidal properties.

F. M. G. M.

Organic Chemistry.

Theory of the Formation of Ethylene. ROBERT KREMANN (*Monatsh.*, 1910, **31**, 211—220).—Experiments have been made on the reaction between ethylene and sulphuric acid by heating the two together in the proportions 1 : 4 gram-mols. The experiments were conducted in a sealed bulb attached to a manometer, and the mercury adjusted so that the volume was kept constant. At all temperatures up to 110°, slow absorption took place until equilibrium had been established (at 57° $p = 115$, at 99° $p = 240$, and at 107° $p = 270$ mm.). Above 111° absorption took place for a short time, but was followed by a rapid increase of pressure due to secondary reactions, for example, the formation of carbon monoxide and sulphur dioxide. Even at the higher temperatures, it was found possible to minimise the effects of the secondary reactions by allowing the mixture to remain at a lower temperature until a pressure was obtained which was close to that corresponding with the higher temperature, and then to plunge the vessel into the bath at the higher temperature. If the pressure was correct, no diminution occurred, but after some time there was a rapid increase of pressure due to the secondary reactions. The value of Q (the algebraic sum of the heat of formation of 1 gram-mol. of ethyl hydrogen sulphate from the alcohol and acid and the heat of solution of this sulphate in the liquid phase) has been calculated from the equation $\log p_1/T_1 - \log p_2/T_2 = Q/R.T_2 - T_1/T_1T_2$, and has a value of about $-3{\cdot}4$ Cal.

Similar experiments have been made by heating ethyl hydrogen sulphate (1 mol.) with sulphuric acid (3 mols.), but experimental difficulties were experienced owing to the secondary reactions. At 99° the pressure rose rapidly at the beginning, then more slowly, remained constant for a short time, and again increased, probably owing to the secondary reactions which are facilitated by the catalytic influence of the carbon formed during the reaction.

The results agree with the view that alcohol and sulphuric acid react instantaneously, forming water and ethyl hydrogen sulphate, and that the latter then decomposes into ethylene and sulphuric acid.

J. J. S.

Preparation of Organic Iodides from the Corresponding Bromides and Chlorides. HANS FINKELSTEIN (*Ber.*, 1910, **43**, 1528—1532. Compare Perkin and Duppa, *Annalen*, 1859, **112**, 125; von Romburgh, Abstr., 1883, 303).—One of the best methods of replacing the chlorine or bromine of an organic compound by iodine is to treat with an acetone solution of sodium iodide. In many cases the reaction is instantaneous, and in all cases where reaction proceeds, a precipitate of sodium chloride or bromide is formed.

The relative reactivities of halogen derivatives towards sodium iodide do not appear to be the same as their reactivities towards

water or methyl alcohol; thus primary alkyl bromides react most readily with sodium iodide, and the tertiary least readily.

The method does not work with acyl chlorides or with chloro- or bromo-compounds, which yield unstable iodo-derivatives. This is usually the case with compounds containing several carbonyl, carboxyl, or phenyl groups; in such cases one of the following changes occurs: (1) Formation of an ethylene linking, for example, $\alpha\beta$-dibromo-β-phenylpropionic acid yields cinnamic acid; (2) ring formation, for example, tetrabromo-*o*-xylene, $C_6H_4(CHBr_2)_2$, yields the compound $C_6H_4<\begin{matrix}CHBr\\|\\CHBr\end{matrix}$; (3) union of two molecules, for example, ethyl bromomalonate yields ethyl ethanetetracarboxylate. Ethyl dibromomalonate yields ethyl ethylenetetracarboxylate. Benzophenone chloride yields dichlorotetraphenylethane, and benzophenone bromide yields tetraphenylethylene.

The following iodo-compounds have been prepared:

Amyl iodide, *iso*propyl iodide, trimethylene iodide, ethyl iodoacetate, *p*-nitrobenzyl iodide, *o*-, *m*-, and *p*-xylylene iodides. J. J. S.

Constitution of the Alcohols arising from the Condensation of Secondary Alcohols with their Sodium Derivatives. MARCEL GUERBET (*Compt. rend.*, 1910, **150**, 979—981. Compare Abstr., 1901, i, 307; this vol., i, 149).—The constitution of certain alcohols described in previous communications has been established by a study of their oxidation products. Dioctyl alcohol is shown to be η-methylpentadecan-ι-ol. *η-Methylpentadecan-ι-one* has b. p. 172—174°/21 mm., D 0·846, and forms a *semicarbazone*, m. p. 195—197° (corr.). Tri*sec*.-butyl alcohol is γ-methyl-ϵ-ethylnonan-η-ol. W. O. W.

Action of Organo-magnesium Compounds on Tiglic Aldehyde and the Optical Behaviour of the Products. PAUL ABELMANN (*Ber.*, 1910, **43**, 1574—1588).—A number of unsaturated alcohols have been prepared by dropping tiglic aldehyde into an ethereal solution of magnesium ethyl bromide or the corresponding ethyl, propyl, *iso*propyl, *iso*butyl, or *iso*amyl bromides, and hydrolysing the resulting products. The yields vary from 40 to 70%. These alcohols can be transformed into the corresponding chlorides by boiling with concentrated hydrochloric acid according to Norris's method (Abstr., 1907, i, 1034), and into diolefine hydrocarbons,

$$CHMe\!:\!CMe\cdot CH\!:\!CHR,$$

by heating with potassium hydrogen sulphate or acetic anhydride and sodium acetate. The same hydrocarbons are formed by the action of quinoline on the chlorides, or by boiling the alcohols with hydrobromic acid. All the hydrocarbons are characterised by a high exaltation in their molecular refractions.

γ-Methyl-Δ^{β}-pentene-δ-ol, CHMe:CMe·CHMe·OH, has b. p. 55—56°/20 mm. or 84—86°/88 mm., or at 139—141°/760 mm. (slight decomp.). It has D^0 0·8793 and $n_D^{17.5}$ 1·4428. The *acetate* has b. p. 153—155°, and the *chloride*, $C_6H_{11}Cl$, b. p. 41—43°/31 mm. *γ-Methylpentane-$\beta\gamma\delta$-triol*, OH·CHMe·CMe(OH)·CHMe·OH, obtained

by oxidising the alcohol with dilute permanganate, has b. p. 133—135°/13 mm. or 159—160°/41 mm., and solidifies when kept. The *triacetyl* derivative, $C_{12}H_{20}O_6$, has m. p. 123° and b. p. 143—146°/16 mm.

γ-Methyl-Δ^β-hexene-δ-ol, CHMe:CMe·CHEt·OH, has b. p. 71—73°/28 mm., 94—95°/80 mm., or 154—155°/760 mm., D^0 0·8857 and n_D^{10} 1·44914. The *acetate* has b. p. 167—170°, and the *chloride*, $C_7H_{13}Cl$, b. p. 51°/11·5 mm.

γ-Methylhexane-βγδ-triol, OH·CHMe·CMe(OH)·CHEt·OH, has b. p. 163°/36 mm., and yields a *triacetate*, $C_{13}H_{22}O_6$, b. p. 146—147°/12 mm.

γ-Methyl-Δ^β-heptene-δ-ol, CHMe:CMe·CPr·OH, has b. p. 74—77°/17 mm., D^0 0·8814, and n_D^{10} 1·45614. The *acetyl* derivative, $C_{10}H_{18}O_2$, has b. p. 79—83°/16 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 53—54°/11 mm.

γε-Dimethyl-Δ^β-hexene-δ-ol, CHMe:CMe·CH(OH)·$CHMe_2$, has b. p. 66—71°/19 mm. or 86—88°/42 mm., D^0 0·8727, and n_D^{10} 1·45214. The *acetate*, $C_{10}H_{18}O_2$, has b. p. 103—106°/57 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 58—60°/21 mm.

γζ-Dimethyl-Δ^β-heptene-δ-ol, CHMe:CMe·CH(OH)·CH_2·$CHMe_2$, has b. p. 113—114°/70 mm., D^0 0·8753, and $n_D^{9.6}$ 1·45337. The *acetate*, $C_{11}H_{20}O_2$, has b. p. 92—95°/18 mm., and the *chloride*, $C_9H_{17}Cl$, b. p. 59—63°/9 mm.

γη-Dimethyl-Δ^β-octene-δ-ol, CHMe:CMe·CH(OH)·CH_2·CH_2·$CHMe_2$, has b. p. 113—114°/30 mm., D^0 0·8762, and n_D^{10} 1·45460. The *acetate*, $C_{12}H_{22}O_2$, has b. p. 159—163°/80 mm., and the *chloride*, $C_{10}H_{19}Cl$, b. p. 83—84°/12 mm.

γ-Methyl-Δ^{βδ}-pentadiene, CHMe:CMe·CH:CH_2, has b. p. 76—79°, D^0 0·7576, and $n_D^{16.5}$ 1·45427

αβγδ-Tetrabromo-γ-methylpentane, CHBrMe·CBrMe·CHBr·CH_2Br, is an unstable liquid, as is also the *dihydrobromide*, $C_6H_{12}Br_2$.

γ-Methyl-Δ^{βδ}-hexadiene, CHMe:CMe·CH:CHMe, has b. p. 107—108°, D^0 0·7753, n_D^{15} 1·46146; *γ-methyl-Δ^{βδ}-heptadiene*,

CHMe:CMe·CH:CHEt,

has b. p. 132—135°, D^0 0·7783, and $n_D^{14.7}$ 1·46493. The *dihydrobromide*, $C_8H_{16}Br_2$, has b. p. 109—110°/16 mm. *γε-Dimethyl-Δ^{βδ}-hexadiene*, CHMe:CMe·CH:CMe_2, has b. p. 114—115°, D^0 0·7714, and $n_D^{16.5}$ 1·45457; the *dihydrobromide*, $C_8H_{16}Br_2$, has b. p. 99—103°/16 mm.

γζ Dimethyl-Δ^{βδ} heptadiene, CHMe:CMe·CH:CH·$CHMe_2$, has b. p. 144—146°, D^0 0·7853, and n_D^{14} 1·46335. The *dihydrobromide*, $C_9H_{18}Br_2$, has b. p. 129—130°/20 mm.

γη-Dimethyl-Δ^{βδ}-octadiene, CHMe:CMe·CH:CH·CH_2·$CHMe_2$, has b. p. 164—167°, D^0 0·7939, and $n_D^{14.5}$ 1·46650. The *dihydrobromide*, $C_{10}H_{20}Br_2$, has b. p. 136—139°/18 mm. J. J. S.

Modification of Couturier and Meunier's Process for the Preparation of Pinacone. A. H. Richard and Paul Langlais (*Bull. Soc. chim.*, 1910, [iv], 7, 454—458).—The process depends on the action of acetone on magnesium amalgam, the compound $Mg<\begin{matrix} O\cdot CMe_2 \\ | \\ O\cdot CMe_2 \end{matrix}$ being first formed, and yielding pinacone hydrate on addition of water (Abstr., 1902, i, 335; 1905, i, 326).

The modification consists in using commercial acetone instead of the pure ketone, and in employing acetone to wash out the pinacone in place of boiling water. It is unnecessary to maintain an atmosphere of dry carbon dioxide in the flask if the process is carried out rapidly. The yield of pinacone varies from 60 to 70% of the theoretical. The other products formed are *iso*propyl alcohol, mesityl oxide, *iso*phorone, a viscous *dihydric alcohol*, $C_6H_{14}O_2$, b. p. 100—108°/17 mm. or 196°/760 mm., and a *trihydric alcohol* (*βγε-trimethylhexan-βγε-triol*), $OH·CMe_2·CMe(OH)·CH_2·CMe_2·OH$, b. p. 150—155°/20 mm., which has been synthesised by Bouveault and Levallois by the action of magnesium methyl iodide on methyl citramalate.

The exact working conditions and particulars of the isolation of these products are given in the original. T A. H.

Oxidation of Δγ-Acetylenic Glycols. Synthesis of α-Hydroxy-acids. GEORGES DUPONT (*Compt. rend.*, 1910, **150**, 1523—1525. Compare this vol., i, 85).—Oxidation of Δγ-acetylenic glycols of the type HO·CRR'·C:C·CRR'·OH by means of potassium permanganate results in the formation of α-hydroxy-acids; the yields, however, are not good, since further oxidation takes place, resulting, with tertiary glycols, in the production of oxalic acid and a ketone.

βε-Dimethyl-Δγ-hexinen-βε-diol yields α-hydroxy*iso*butyric acid, whilst *ββεε-tetraphenyl-Δγ-butinen-βε-diol*, $OH·CPh_2·C:C·CPh_2·OH$, m. p. 149—150°, obtained by the action of benzophenone on magnesium acetylene dibromide, gives diphenylglycollic acid with oxalic acid and benzophenone.

The yields are improved by employing the diacetates of the glycols. W. O. W.

Alkaline Hydrolysis of Glyceryl Trinitrate. ERNST BERL and MAX DELPY (*Ber.*, 1910, **43**, 1421—1429).—The authors have hydrolysed an alcoholic solution of glyceryl trinitrate at 4° with alcoholic potassium hydroxide, and from the products have obtained ammonia, potassium nitrite and nitrate, carbon dioxide, hydrogen cyanide, oxalic acid, mesoxalic acid, αα-glyceryl dinitrate, and unchanged glyceryl trinitrate. C. S.

General Method for the Direct Preparation of Thiols from Alcohols by Catalysis. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, **150**, 1217—1221. Compare this vol., i, 294).—When the vapour of an alcohol mixed with hydrogen sulphide is passed over heated thorium oxide, a thiol is produced; the reaction is represented as: (1) $ThO_2 + 2C_nH_{2n+1}·OH = ThO(OC_nH_{2n+1})_2 + H_2O$; (2) $ThO(OC_nH_{2n+1})_2 + 2H_2S = ThO_2 + 2C_nH_{2n+1}·HS + H_2O$. A sulphide is formed in small quantity and with greater difficulty: $ThO(OC_nH_{2n+1})_2 + 2C_nH_{2n+1}·HS = ThO_2 + 2(C_nH_{2n+1})_2S + H_2O$. The thorium oxide acts as a catalyst, and the action is continuous. The hydrogen sulphide employed need not be free from hydrogen.

An excellent yield of the corresponding thiols has been obtained from methyl, ethyl, propyl, *iso*butyl, *iso*amyl, and allyl alcohols, keeping the catalyst at 300—360°. Benzyl alcohol gave a good yield of

thiol, accompanied by the normal sulphide and some stilbene. In the case of secondary alcohols, the yields are less satisfactory; the following compounds have been prepared: propan-β-thiol; *cyclo*hexanethiol, b. p. 155° (compare Mailhe and Murat, this vol., i, 374); 2-*methyl*cyclo*hexanethiol*, b. p. 161°; 3-methyl*cyclo*hexanethiol, b. p. 168°; 4-*methyl*cyclo*hexanethiol*, b. p. 169°.

Thiophenols may be prepared by this method at 430—480°, but in no case does the yield exceed 17%. At 450°, phenol gives a small amount of diphenyl ether. W. O. W.

Formation of Acetic and Formic Acids by the Hydrolysis of Substances Containing Lignin. WILLIAM E. CROSS (*Ber.*, 1910, **43**, 1526—1528).—Acetic and formic acids are produced when substances rich in lignin are hydrolysed with 1% sulphuric acid at 130°, or even 110°.

The substances used were straw, jute, and various woods. Cellulose does not yield volatile acids, and pentosans but very little, so that the acids come from the lignin. It would thus appear that lignin contains acetyl and formyl groups, in addition to methoxy-groups.

With pine wood, the ratio acetic : formic acid is 4 : 1. J. J. S.

Simple Preparation of a Crystalline Ferric Acetate. RUDOLF F. WEINLAND and ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1910, **67**, 250—252).—When concentrated solutions of ferric chloride (1 mol.) and sodium acetate (3 mols.) are mixed and allowed to evaporate slowly, large, dark red prisms of ferric acetate are obtained. The addition of sodium platinichloride produces a characteristic precipitate of hexa-acetotriferric platinichloride (this vol., i, 296). The red salt is a compound of the mono- and di-acetate of this base:

$$\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]OAc,\left[Fe_3\begin{matrix}(OAc)_3\\OH_2\\OH\end{matrix}\right](OAc)_2,2H_2O.$$

Lithium chloride forms with this solution a *salt*:

$$2\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]Cl,\left[Fe_2\begin{matrix}(OAc)_6\\OH_2\\OH\end{matrix}\right](OAc)_2,14H_2O.$$

C. H. D.

Mixed Compounds of Salts and Anhydrides of Fatty Acids. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1910, [iv], **7**, 461—464).—Franzen has shown (Abstr., 1908, i, 937) that compounds, analogous to Gerhardt's compound of potassium acetate and acetic anhydride, may be obtained with other acetates, and that for sodium and potassium two series of such products exist, represented by the formulæ: $Ac_2O,2CH_3{\cdot}CO_2M'$ and $Ac_2O,CH_3{\cdot}CO_2M'$. It is now shown that compounds analogous with those represented by the second formula may be obtained with acetic anhydride and the salts of the homologues of acetic acid, but that compounds represented by the first formula are not obtainable in these cases. The substances obtained crystallise

well, possess rhombic symmetry, and show marked double refraction. On exposure to the air, the crystals are transformed in a few minutes into microscopic cubes, and, when warmed at 80°, become isotropic without losing their form. The isotropic crystals melt at 150°; on further heating, the liquor effervesces and then passes into anisotropic crystals, which finally change at a higher temperature into amorphous solids. The original compounds probably have the general formula $Ac_2O{:}O(CO{\cdot}R)M'$, and the first change from anisotropic to isotropic crystals probably accompanies a change represented by the equation: $R{\cdot}CO_2M'(CH_3CO)_2O \longrightarrow (R{\cdot}CO_2M')_2(CH_3CO)_2O$. The substances are obtained by boiling the appropriate salt with acetic anhydride during twenty minutes, filtering, and cooling, when colourless needles of the desired products are deposited. *Compounds* with the following salts are described.

Sodium formate.—This softens and becomes opaque at 82°, begins to clear at 114°, melts at 154°, effervesces at 174°, and re-solidifies at 185°. *Sodium propionate.*—This softens at 80°, melts at 154°, effervesces at 174°, and re-solidifies at 185°. *Sodium butyrate.*—This melts at 155°, effervesces at 180°, and re-solidifies at 188—190°.

Sodium valerate.—This, on heating, undergoes the series of changes mentioned under sodium formate at the following corresponding temperatures 82°, 154°, 175°, 180°. Exposed to the air this compound forms a mixture of isotropic cubes, crystalline substances, and isotropic droplets; the last of these eventually form monoclinic crystals showing extinction at about 45°, and analogous to sodium acetate crystals.

T. A. H.

Preparation of Pivalic Acid. A. H. RICHARD and P. LANGLAIS (*Bull. Soc. chim.*, 1910, [iv], 7, 464—468).—Tiemann and Semmler have shown (Abstr., 1898, i, 629) that methyl ketones on oxidation by sodium hypobromite furnish bromoform and acids containing one carbon atom less than the parent ketones, and Denigès has confirmed this behaviour for pinacolin (Abstr., 1903, i, 606). This process has now been applied to pinacolin for the preparation of pivalic acid, of which a yield equal to 70% of the theoretical was obtained. Full details of the method of preparation are given in the original. The by-products are unchanged pinacolin, bromoform, carbon tetrabromide, tribromopinacolin, and trimethyl-lactic acid. The last-mentioned substance probably originates through the formation of some dibromopinacolin, which by the action of alkali would pass into trimethylpyruvic acid, and this, by the further action of alkali, would furnish trimethyl-lactic acid (compare Wittorff, Abstr., 1900, i, 422), and a trial with dibromopinacolin under the conditions prescribed confirmed this view. Boeseken has described already this method of preparing pivalic acid, but his observation that *iso*butyric acid is a by-product could not be confirmed.

T. A. H.

Some Salts of Gallipharic Acid, a Fatty Acid obtained by the Oxidation of *cyclo*Gallipharic Acid. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Arch. Pharm.*, 1910, 248, 294—302).—An examination of the following salts of gallipharic acid confirms the

supposition previously advanced (Abstr., 1904, i, 587), that this acid is a pentadecanecarboxylic acid, $C_{15}H_{31}\cdot CO_2H$. *Sodium* salt, $C_{16}H_{31}O_2Na$; *potassium* salt; *potassium hydrogen* salt, $C_{16}H_{31}O_2K,C_{16}H_{32}O_2$, m. p. 103°; *calcium* and *barium* salts; *calcium hydrogen* salt, $(C_{16}H_{31}O_2)_2Ca,2C_{16}H_{32}O_2$, m. p. 87°; *barium hydrogen* salt,

$$(C_{16}H_{31}O_2)_2Ba,2C_{16}H_{32}O_2,$$

m. p. 98°; *cadmium* salt, m. p. 125—140°; *cadmium hydrogen* salt, $(C_{16}H_{31}O_2)_2Cd,2C_{16}H_{32}O_2$, m. p. 98·5°; *silver* salt; *silver hydrogen* salt, $2C_{16}H_{31}O_2Ag,C_{16}H_{32}O_2$; *copper* salt; *copper hydrogen* salt,

$$(C_{16}H_{31}O_2)_2Cu,C_{16}H_{32}O_2,$$

m. p. 98°; *ferric* salt, m. p. 78°; basic *lead* salt,

$$10(C_{16}H_{31}O_2)_2Pb,Pb(OH)_2.$$

C. S.

Isomerisation of Oleic Acid by Displacement of the Double Linking. ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1910, **150**, 1525—1528).—The reaction of Saytzeff (Abstr., 1887, 386), in which oleic acid is treated with hydrogen iodide and the product boiled with alcoholic potassium hydroxide, gives rise to a mixture containing at least four acids. In addition to regenerated oleic acid there is formed hydroxystearic acid, m. p. 83—84°, Δ^{η}-*elaidic acid*, and Δ^{θ}-elaidic acid. The separation of these acids is described, and Saytzeff's *iso*oleic acid shown to be a mixture.

Δ^{η}-Elaidic acid has also been obtained by partial hydrogenation of the corresponding stearolic acid by the method described previously (this vol., i, 356). The compound occurs in tablets, m. p. 53°, and yields a *dihydroxystearic acid*, crystallising in elongated laminæ, m. p. 98·5°. W. O. W.

Two New Isomerides of Stearolic Acid. ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1910, **150**, 1245—1247. Compare Abstr., 1909, i, 630; this vol., i, 356).—When fused stearolic acid is saturated with hydrogen iodide an oily mixture containing two isomeric di-iodostearic acids is produced. On hydrolysis this yields the original stearolic acid, together with two new isomerides crystallising in pearly lamellæ, and a monoiodo-acid, which resists further hydrolysis. Δ^{η}-*Stearolic acid*, m. p. 47·5°, yields suberic acid on oxidation, and unites with iodine, forming $\theta\iota$-*di-iodoelaidic acid*, needles, m. p. 67°. Δ^{ι}-*Stearolic acid*, m. p. 47°, yields sebacic acid on oxidation, and furnishes $\iota\kappa$-*di-iodoelaidic acid*, lamellæ, m. p. 45°; κ-*ketostearic acid* crystallises in rhombic lamellæ, m. p. 73·5°.

The iodoelaidic acids, m. p. 23—24° and 39°, described in a previous paper are now shown to be θ-iodo-Δ^{θ}-elaidic acid and ι-iodo-Δ^{θ}-elaidic acid respectively. W. O. W.

Preparation of Aqueous Soluble Compounds from the Anhydrides of Hydroxymercurycarboxylic Acids. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 221483).—When the hydroxymercurycarboxylic anhydrides of the general formula

$$\underline{Hg\cdot A\cdot CO\cdot O},$$

where A is an aliphatic or aromatic residue, are slowly added to an aqueous solution containing molecular equivalents of alkali sulphite,

thiosulphate, or hyposulphite, and the mixture evaporated under reduced pressure, soluble products which are suitable for therapeutic employment are obtained.

The *product*, $ONa\cdot SO_2\cdot S\cdot Hg\cdot CH_2\cdot CO_2Na$, from hydroxymercury-acetic anhydride and sodium thiosulphate contains 48·07% Hg, whilst hydroxymercurybenzoic anhydride and sodium sulphite yield the *compound*, $NaO\cdot SO_2\cdot Hg\cdot C_6H_4\cdot CO_2Na$, containing 44·84% Hg.

F. M. G. M.

Action of Halogen Acids on Glycidic Esters. GEORGES DARZENS (*Compt. rend.*, 1910, **150**, 1243—1245. Compare Abstr., 1905, i, 116).—Hydrogen chloride combines with ethyl ββ-dimethylglycidate in cold ethereal solution, forming *ethyl β-chloro-α-hydroxy-*iso*valerate*, $C_7H_{13}O_3Cl$, a substance with an unpleasant odour, m. p. 31—32°, b. p. 96—98°/20 mm. Ethyl αββ-trimethylglycidate and hydrogen chloride form *ethyl β-chloro-α-hydroxy-α-methyl*iso*valerate*, $C_8H_{15}O_3Cl$, b. p. 104—106°/21 mm. Hydrogen bromide yields the corresponding *bromo*-derivative, m. p. 21—22°, b. p. 100—105°/18 mm.

Hydrogen iodide converts glycidic esters into esters of the corresponding unsaturated acids; thus, ethyl ββ-dimethylglycidate undergoes reduction to dimethylacrylic acid. It is essential for the success of the foregoing reactions that the materials should be perfectly dry.

W. O. W.

Action of Ethyl Sodiomalonate on ακ-Dibromodecane. ADOLF FRANKE and OSWALD HANKAM (*Monatsh.*, 1910, **31**, 177—189). —ακ-Dibromodecane reacts with ethyl sodiomalonate, yielding a product which appears to be ethyl *cyclo*undecane-1 : 1-dicarboxylate, $\begin{matrix} CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>\!C(CO_2Et)_2$. A by-product, formed at the same time, appears to be ethyl dodecanetetracarboxylate,

$$CH(CO_2Et)_2\cdot [CH_2]_{10}\cdot CH(CO_2Et)_2.$$

Decane-ακ-diol, prepared by Bouveault and Blanc's method (Abstr., 1903, i, 731), reacts with fuming hydrobromic acid at 60° in sealed tubes, yielding *ακ-dibromodecane*, $C_{10}H_{20}Br_2$, which crystallises in colourless plates, m. p. 27°.

Ethyl cyclo*undecanedicarboxylate*, $C_{17}H_{30}O_4$, is a colourless, viscid liquid, b. p. 200—220° under reduced pressure. The corresponding *acid*, $C_{13}H_{22}O_4$, forms a fatty solid, m. p. 75°, and does not combine with bromine; the *potassium* salt is gelatinous, and the *silver* and *calcium* salts form colourless precipitates.

When heated at 130—150° the dibasic acid loses carbon dioxide and yields cyclo*undecanecarboxylic acid*, $C_{11}H_{21}\cdot CO_2H$, which is also a fatty solid, m. p. 94—96°.

Ethyl dodecanetetracarboxylate, $C_{24}H_{42}O_8$, has b. p. 250—265° under reduced pressure; the corresponding *acid*, $C_{16}H_{26}O_8$, crystallises from water, and has m. p. 128°, but when heated at 160—170° loses carbon dioxide and yields *dodecanedicarboxylic acid*, $CO_2H\cdot C_{12}H_{24}\cdot CO_2H$, which also crystallises from water, and has m. p. 123°.

J. J. S.

Arabonic Acid. K. H. BÖDDENER and BERNHARD TOLLENS (*Ber.*, 1910, **43**, 1645—1650 *).—Guerbet's method of obtaining *d*-arabinose

* and *Zeitsch. Ver. deut. Zuckerind*, 1910, 727—738.

by heating a solution of mercuric gluconate (Abstr., 1908, i, 123) has been applied to mercuric *l*-arabonate, whereby a poor yield of *l*-erythrose has been obtained.

A freshly prepared solution of arabonolactone has $[\alpha]_D$ about 70°, and one of arabonic acid has $[\alpha]_D$ $-10°$; both solutions in course of time attain to the same value, $[\alpha]_D$ $-51·5°$. This behaviour, which is also exhibited by gluconic acid, galactonic acid, rhamnonic acid, and their lactones, appears to be a characteristic property of acids of the sugar group, and can be utilised for their identification.

Methyl arabonate, obtained by keeping a solution of arabonolactone in somewhat diluted methyl alcohol over lime or by heating calcium arabonate, methyl alcohol, and sulphuric acid on the water-bath, exhibits an initial rotation, $[\alpha]_D$ $-6·7°$, which changes to $-42·7°$ by keeping, the change being due to the gradual decomposition of the ester into the acid and methyl alcohol. C. S.

Formation of Lævulic Acid from Hexoses. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 387—390).—There are two stages in the formation of lævulic acid from hexoses: hydroxymethylfurfuraldehyde is first formed by elimination of water, and is subsequently transformed into lævulic acid and formic acid. Ihl and Pechmann's test for hexoses is explained by the fact that warming hydroxymethylfurfuraldehyde with diphenylamine yields a substance of dark blue colour. A. J. W.

Action of the Electric Discharge on Acetaldehyde in Presence of Hydrogen. ADOLPHE BESSON and A. FOURNIER (*Compt. rend.*, 1910, 150, 1238—1241. Compare Losanitsch, this vol., i, 1).—When the vapour of acetaldehyde mixed with a small amount of hydrogen is submitted to the action of the silent electric discharge, a brilliant phosphorescence is produced, and a liquid formed having an odour of pickled herrings. This has been found to contain acetic acid and homologous acids, acetone, diethyl ketone, diacetyl, unidentified viscous substances, and an acid, $C_4H_8O_3$, having the properties of β-hydroxybutyric acid. W. O. W.

α-Bromocrotonaldehyde. P. L. VIGUIER (*Compt. rend.*, 1910, 150, 1431—1433. Compare Abstr., 1909, i, 691).—The constitution of α-bromocrotonaldehyde has been proved by its oxidation to α-bromocrotonic acid. A more rapid method for preparing the substance than that previously described consists in brominating crotonaldehyde and adding the product to a 50% solution of sodium acetate at 150—170°. The aldehyde is separated by distillation in steam. When heated with pyridine and malonic acid, it yields *γ-bromosorbic acid*,

$$CHMe:CBr·CH:CH·CO_2H,$$

m. p. 133°; the *potassium* salt forms pearly lamellæ (compare Riedel and Straube, Abstr., 1909, i, 550). The cyanohydrin decomposes when distilled in a vacuum; on hydrolysis, it yields *β-bromo-α-hydroxy-Δ^β-pentenoic acid*, $CHMe:CBr·CH(OH)·CO_2H$, m. p. 123—124°; the *potassium* salt crystallises in prisms, the *silver* salt in long, brilliant needles. W. O. W.

Production of Aldehyde Resins by the Carbonisation of Wood in Closed Vessels. René P. Duchemin (*Bull. Soc. chim.*, 1910, [iv], 7, 473—479).—A résumé is first given of the work of Kleeberg (Abstr., 1891, 1199), Trillat (*Annalen*, 1891, **263**, 312), Blumer (Fr. Pat. 329982 of 1903), Delaire (Fr. Pat. 361509 of 1905), Baekeland (*Mon. Sci.*, 1909, 421) and others on the condensation of formaldehyde with phenols in the presence of alkalis or acids to form resinous products, which in some cases resemble copal or lac.

In connexion with the investigation of a new process of manufacturing crude acetates (Fr. Pat. 375314 and 402907 of 1908), the author has observed the formation of similar resins in passing the acid vapours from the distillation of wood, first through an apparatus for the removal of tar, and then into scrubbers containing alkaline liquids. The latter are at first brown or black, but become golden-yellow as the passage of the vapours continues, and finally deposit black, plastic masses, which after heating at 200° become hard and possess a conchoidal fracture. Similar products are obtained by (1) heating crude pyroligneous acid under a reflux condenser, (2) condensing "heavy oils" recovered from crude pyroligneous acid with formaldehyde in presence of hydrochloric acid, (3) heating the mother liquors recovered from the manufacture of crude acetates, and then adding water. These products have m. p. 60—70°, dissolve in alkaline solutions, and are re-precipitated by acids. They are soluble in acetone, wood-spirit, or methyl acetate, but the extent of their solubility depends on the temperature to which they have been heated. These resins probably result from the interaction of aldehydic with phenolic substances, both these groups of products occurring in the vapours from the distillation of wood. It is suggested that wood tar may consist of a solution of these resins in phenols (compare Lingner, Fr. Pat. 328971 of 1903).

The resins obtained in distilling wood-spirit over alkalis differ from the foregoing in their lighter colour and in being insoluble in alkalis.

T. A. H.

Preparation of Pinacolin. A. H. Richard and P. Langlais (*Bull. Soc. chim.*, 1910, [iv], 7, 459—461).—The preparation was effected (1) by heating pinacone hydrate with a 30% solution of sulphuric acid during three hours at 150° and steam-distilling the mixture, or (2) by heating pinacone hydrate with dry oxalic acid in a calcium chloride bath. The first process gave a 90%, and the second a 75% yield of crude pinacolin. The oxalic acid was used several times, but eventually became coated with tarry matters and had to be replaced by fresh material.

On fractionation, the crude pinacolin yielded, as more volatile by-products, acetone and di*iso*propenyl (Couturier, Abstr., 1893, i, 244; Kondakoff, Abstr., 1901, i, 62), and, as less volatile by-products, unaltered pinacone, mesityl oxide, and *iso*phorone. The di*iso*propenyl probably resulted from complete dehydration of pinacone, but the mesityl oxide and *iso*phorone were probably present as impurities in the pinacone hydrate used (see this vol., i, 455), and the acetone and a

small quantity of mesitylene found probably resulted from the action of acids on these impurities. T. A. H.

Reduction of Aliphatic Diketones. EDMOND E. BLAISE and A. KŒHLER (*Bull. Soc. chim.*, 1910, [iv], **7**, 416—420).—In a previous paper (Abstr., 1909, i, 204) it has been shown that aliphatic diketones can be synthesised by the action of the chlorides of dibasic acids on mixed organic compounds of zinc. Perkin has observed (Trans., 1891, **59**, 214) that nonane-$\beta\theta$-dione on reduction with sodium yielded a cyclic pinacone, and it was therefore of interest to ascertain within what limits the formation of a ring depends on the relative positions of the two carbonyl groups. Reduction of octane-$\beta\eta$-dione, decane-$\gamma\theta$-dione, and undecane-$\gamma\iota$-dione furnished no cyclic pinacones, but only the corresponding glycols, and, similarly, attempts to dehydrate undecane-$\gamma\iota$-diol were unsuccessful.

Octane-$\beta\eta$-dione, on reduction by Perkin's method (*loc. cit.*), yielded the secondary cyclic alcohol already described by Perkin (Trans., 1890, **57**, 245), and *octane-$\beta\eta$-diol*, b. p. 138—139°/15 mm., a viscous liquid with a sweetish acrid taste, and readily soluble in organic solvents; its *diphenylurethane*, m. p. 126°, crystallises in long needles from a mixture of light petroleum and ether.

Decane-$\gamma\theta$-dione under similar conditions yielded a *hydrocarbon*, b. p. 70—72°/11 mm., and the corresponding *glycol*, m. p. 72°, which crystallises in silky needles from a mixture of ether and light petroleum. The *diphenylurethane*, m. p. 137°, crystallises from ether in needles, and is greasy to the touch. Undecane-$\gamma\iota$-dione furnished a trace of pinacone (?), b. p. 156°/18 mm., and the corresponding *glycol*, m. p. 80·5°, crystallising from warm ether in long, silky needles. The *diphenylurethane*, m. p. 84—85° (approx.), crystallises from a mixture of benzene and light petroleum in splendid needles. T. A. H.

New Synthesis of Natural and Racemic Erythritol. H. PARISELLE (*Compt. rend.*, 1910, **150**, 1343—1346. Compare Abstr., 1909, i, 691; Lespieau, Abstr., 1907, i, 173).—Δ^{α}-Butylene-$\gamma\delta$-oxide, $\begin{matrix}CH_2\\ | \\ O\end{matrix}\!\!>CH\cdot CH{:}CH_2$, prepared by heating δ-bromo-Δ^{α}-butylene oxide with potassium hydroxide, is a very mobile liquid, b. p. 70°/760 mm., D^0 0·9006, D^{20} 0·87, n_D^{20} 1·416. When shaken with water and a few drops of sulphuric acid, a solid polymeride is formed, and the solution, on distillation in a vacuum, yields erythrol (Δ^{α}-butylene-$\gamma\delta$-diol), $OH\cdot CH_2\cdot CH(OH)\cdot CH{:}CH_2$, as a syrupy liquid, b. p. 91—93°/12 mm., D^{14} 1·05, n_D^{14} 1·469; the *diphenylurethane* has m. p. 125—126°. When the diol is treated with barium permanganate, a syrup is obtained, which deposits natural erythritol when sown with a crystal of this substance. The residual liquid contains racemic erythritol, isolated and identified by conversion into the dibenzoylacetal. W. O. W.

Aloinose, the Sugar from Aloin. EUGÈNE LEGER (*Compt. rend.*, 1910, **150**, 983—986; *Bull. Soc. chim.*, 1910, [iv], **7**, 479—485. Compare Abstr., 1903, i, 356; 1904, i, 907).—Further experimental

details are given for the preparation of aloinose from barbaloin. The sugar has $[\alpha]_D$ 57·3° to 58·5°, and forms an *osazone*, crystallising in elongated, pointed lamellæ.

On hydrolysis with alcoholic sulphuric acid, nataloin yields small quantities of a non-crystalline, lævorotatory sugar closely resembling aloinose. W. O. W.

Nitration of Cotton Wool. Cellulose. PIEST (*Zeitsch. angew. Chem.*, 1910, 23, 1009—1018).—A résumé of previous work on cellulose and its nitrates is given. The action of various alkalis on gun-cottons prepared in different ways has been investigated.

Gun-cotton prepared from cotton wool treated in the usual manner gave a residue of 8% when left in contact with 0·5*N*-sodium hydroxide solution during ten days, whereas a gun-cotton prepared from a strongly bleached cotton wool left a residue of only 1·7% insoluble matter, after similar treatment during four days. Gun-cotton prepared from mercerised cotton gave a residue of 13% after ten days. Similar experiments with a concentrated ammonium sulphide solution gave a residue of 49·5% after eight days using ordinary gun-cotton, a residue of 37·5% with gun-cotton from strongly bleached cotton, and 52% with a gun-cotton from mercerised cotton. Treatment of a gun-cotton with alkalis affords a method for determining the manner in which the cotton had been treated before nitration.

The resistance of various gun-cottons towards alkalis is in the order of the resistance of the materials from which they were obtained.

The action of alkalis on collodion wools prepared from samples of cotton wool which have been subjected to different treatment has also been examined, and the results obtained are similar to those with gun-cottons. When concentrated ammonium sulphide is used, complete hydrolysis is brought about in four days, since the residue left contains no nitrogen.

During nitration, especially when the amount of water present is large, hydroxycelluloses are formed, and the final products are mixtures of esters of cellulose and hydroxycelluloses.

Treatment of the esters with ammonium sulphide appears to bring about a partial conversion of cellulose into hydroxycelluloses.

J. J. S.

Mercury Fulminate. ANDREAS SOLONINA (*Zeitsch. Schiess Sprengstoffwesen*, 1910, 5, 41—46, 67—72).—A discussion of the various methods usually employed for the preparation of mercury fulminate, with particulars of numerous experiments by the author, and microphotographs showing the crystalline structure of the products.

The second paper contains details of experiments for the purification of mercury fulminate for analysis; the employment of ammonia is not considered satisfactory, but the preparation of the crystalline compound with pyridine, its subsequent decomposition with water, and the final estimation of mercury by electrolysis is recommended.

F. M. G. M.

Calcium Cyanamide and some Compounds Prepared from it. FR. REIS (*Biochem. Zeitsch.*, 1910, **25**, 460—476).—Cyanamide in a state of purity is best prepared from calcium cyanamide by precipitation with the theoretical quantity of oxalic acid calculated from the calcium content of the calcium cyanamide. An alkaline solution of calcium cyanamide rapidly decomposes at the ordinary temperature, and still more rapidly on heating, dicyanodiamide in varying amounts being formed; an acid solution is, at the ordinary temperature, stable. Warm permanganate solution has practically no action; Devarda's alloy reduces the cyanamide rapidly to ammonia, and gives a large increase in the quantity of dicyanodiamide formed. The optimum conditions for the conversion into dicyanodiamide are obtained by the use of carbonates of the alkalis and alkaline earths at 65°. The decomposition undergone in the presence of soil may be due to bacterial action, if the concentration be not so great as to inhibit the action of the organisms. The presence of ferric oxide has the catalytic effect of accelerating the decomposition of cyanamide into carbamide. No compound of cyanamide and iron could be formed. G. S. W.

Cryohydrates of Ammonium and Potassium Thiocyanates. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 423—427). —The author has investigated the cryohydrates of these salts by Flawitzky's method of cooling mixtures. Ammonium thiocyanate forms the cryohydrate, $NH_4·CNS,5·851H_2O$, at $-25·2°$, and the potassium salt, $KCNS,5·349H_2O$, at $-31·2°$; these compositions are in accord with Guthrie's law (this Journ., 1875, 530), the smaller proportion of water present in the cryohydrate corresponding with the lower temperature. The lower water-content of the cryohydrate of the potassium salt is also in agreement with the greater solubility of this salt. In the formation of these cryohydrates, the mixtures of salt and snow do not solidify, and the residues left in the refrigerator always consist solely of the excess of salt which has not taken part in the reaction, so that it is highly probable that the action occurs between the snow and anhydrous salt without formation of hydrates.

The m. p.'s of these thiocyanates were given by Pohl (1851) as 161·2° for the potassium salt and 159° for the ammonium salt, the latter figure being confirmed by Reynolds (this Journ., 1869, 1). The author obtains the m. p. 174·2° for the potassium salt, and 149·5° for the ammonium salt, but in the latter case decomposition occurs to some extent. Using these numbers, Flawitzky's law (Abstr., 1906, ii, 152) gives (1) for the ammonium salt, the relation between the polymerisations of the salt and water represented by $(H_2O)_6 : (NH_4·CNS)_5$, and the composition of the cryohydrate, $NH_4·CNS,5·931H_2O$; and (2) for the potassium salt, the ratio $(H_2O)_4 : (KCNS)_5$, and the composition $KCNS,5·332H_2O$ for the cryohydrate. If potassium and ammonium thiocyanates form a eutectic mixture, the constituents should be present in the proportion of 3 mols. to 2 mols. T. H. P.

Diastatic Scission of Lactose Derivatives. H. BIERRY and ALBERT RANC (*Compt. rend.*, 1910, **150**, 1366—1368. Compare Abstr., 1908, i, 1031).—Lactoseaminoguanidine nitrate (Wolff, Abstr.,

1896, i, 78) has $[\alpha]_D^{20}$ 8·4°, and m. p. 225—227° on the Maquenne block. The digestive juice of snails hydrolyses this substance with formation of galactose and dextroseaminoguanidine. The same ferment decomposes lactosesemicarbazone into galactose and dextrosesemicarbazone, a similar fission occurring in the case of Schoorl's lactosecarbamide (*Rec. trav. chim.*, 1903, **22**, 31).

The experiments support Fischer's view that lactose is the galactoside of dextrose. W. O. W.

Instability of Alloxan. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1910, **32**, 809).—A sample of alloxan, which had been kept for several years in a bottle, suddenly underwent spontaneous decomposition and caused a violent explosion. This behaviour does not appear to have been noticed previously.

MARSTON T. BOGERT (*ibid.*, 809—810) records a similar explosion in a case containing alloxan amongst other fine organic chemicals.

E. G.

Formation of Hydrogen Cyanide. ARMAND JORISSEN (*Bull. Acad. roy. Belg.*, 1910, 224—233).—The first part of the paper deals with the conclusions arrived at by the author and others concerning the production of hydrogen cyanide in plants (compare Jorissen, Abstr., 1885, 181; Jorissen and Hairs, Abstr., 1892, 502; Hébert, Abstr., 1899, ii, 377; Greshoff, Abstr., 1907, ii, 121; and Treub, *Ann. Jar. bot. Buitenzorg*, 1905, [ii], **4**, 86).

Although Seyewetz and Poizat have recently shown (Abstr., 1909, i, 146) that a large number of aromatic compounds give hydrogen cyanide when boiled with a mixture of nitric and nitrous acids, this observation cannot be used in support of the hypothesis that the naturally occurring hydrogen cyanide is formed by the action of nitrates on organic substances, since the conditions are entirely different. The author, however, finds that a number of substances when acted on with dilute nitric acid at the ordinary temperature in the light, form appreciable quantities of hydrogen cyanide; thus when 0·5 to 1·0 gram of morphine, brucine, vanillin, quinol, catechol, resorcinol, sucrose, lactose, or honey is kept in contact with 100 c.c. of a 3·4% aqueous solution of nitric acid at the ordinary temperature and exposed to light, a small amount of hydrogen cyanide is formed. The reaction, like that described by Seyewetz and Poizat, is inhibited by carbamide, but is unaffected by asparagine. Addition of potassium nitrite solution to the nitric acid immediately after the addition of vanillin does not cause the instantaneous formation of hydrogen cyanide. E. H.

Application of Magnesium in Organic Chemistry. VICTOR GRIGNARD (*Chem. Zeit.*, 1910, **34**, 529; *Bull. Soc. chim.*, 1910, [iv], **7**, 453—454).—In reply to Barbier (this vol., i, 308), the author mentions that he has in common with others, who have written on the application of magnesium in organic chemistry, referred to the importance in this connexion of Barbier's synthesis of dimethylheptenol by the use of magnesium methyl iodide. He adds, however,

that Barbier's method is a modification of the Saytzeff reaction, in which two substances merely react in presence of magnesium, whilst his own method is derived from the work of Frankland, Wanklyn, and Wagner on mixed organo-magnesium compounds and their application.

T. A. H.

_cyclo_Hexylallylene [_cyclo_Hexylpropylene] and _cyclo_Hexylpropinene. B. DE RESSÉGUIER (*Bull. Soc. chim.*, 1910, [iv], 7, 431—434).—*cyclo*Hexylpropylene, $C_6H_{11}\cdot CH_2\cdot CH:CH_2$, D^0 0·8312, D^{13} 0·8196, n_D^{13} 1·45362, b. p. 148—149°, prepared by the action of allyl bromide on magnesium *cyclo*hexyl bromide (compare Tiffeneau, Abstr., 1904, i, 872), is a colourless liquid of pleasant odour (compare Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 630). The *dibromide* has D^0 1·537 and b. p. 143—144°/16 mm. On treatment with potassium hydroxide in alcohol, it yields cyclo*hexylbromopropylene*,

$$C_6H_{11}\cdot CH_2\cdot CH:CHBr,$$

D^0 1·2063, b. p. 122—124°/17 mm., a colourless liquid, and finally cyclo*hexylpropinene*, b. p. 165—170°. The latter was not purified, but was converted into the sodium derivative, and the latter by the action of carbon dioxide transformed into cyclo*hexyltetrolic acid*,

$$C_6H_{11}\cdot CH_2\cdot C:C\cdot CO_2H,$$

m. p. 74—75°, which crystallises from carbon tetrachloride. The *methyl* ester has b. p. 135°/15 mm., D^0 1·010, D^{16} 0·9978, n_D^{12} 1·48354, corresponding with mol. ref. 51·41 in place of the calculated value 50·43 (compare Moureu, Abstr., 1906, ii, 1). T. A. H.

Freezing of Mixtures of Isomeric Benzene Derivatives. GIUSEPPE BRUNI (*Zeitsch. Elektrochem.*, 1910, 16, 285).—The phenomena described by Fischer (this vol., i, 309) are quite in accordance with the regularities observed by the author. In general, position isomerides in the benzene series do not form solid solutions, but substances having analogous substituting groups in the same position do.

T. E.

Derivatives of Ethylbenzene and of _iso_Propylbenzene. ERLING SCHREINER (*J. pr. Chem.*, 1910, [ii], 81, 557—564).—*p*-Chloroethylbenzene is readily obtained by heating ethyl bromide and chlorobenzene with aluminium chloride on the water-bath. An individual product is not obtained when bromobenzene is used. *o*- and *p*-Nitroethylbenzene are easily obtained by dissolving ethylbenzene in fuming nitric acid and fractionating the product under diminished pressure. By reduction with tin and hydrochloric acid, each yields the corresponding amino-derivative, from which by diazotisation and treatment with potassium iodide, o-*iodoethylbenzene*, b. p. 226°, D_4^{16} 1·6189, n_D 1·59408, and p-*iodoethylbenzene*, m. p. −11°, b. p. 230°, D_4^{16} 1·6095, n_D^{22} 1·59094, are obtained. The *iododichloride*, $C_6H_4Et\cdot ICl_2$, of the former, obtained by the direct action of chlorine at 0°, is an unstable, yellow, crystalline substance decomposing at 63°; treatment with sodium hydroxide yields, not the iodoso-compound, but the *iodonium hydroxide*, $I(C_6H_4Et)_2\cdot OH$, since the addition of potassium iodide to the solution yields the *iodide*, $(C_6H_4Et)_2I_2$, which decomposes at 126°.

p-Iodo*iso*propylbenzene, which can be prepared by heating *iso*propylbenzene, iodine, and iodic acid in slightly diluted acetic acid for six hours, forms a *iododichloride*, $C_6H_4Pr^{\beta}\cdot ICl_2$, a citron-yellow powder decomposing at 110°, from which the *iodoso*-compound, $C_6H_4Pr^{\beta}\cdot IO$, decomposing at 165° (the *acetate*, $C_6H_4Pr^{\beta}\cdot I(OAc)_2$, has m. p. 89°), the *iodoxy*-compound, exploding at 191°, and the iodonium *iodide*, decomposing at 140°, are readily obtained. C. S.

Phenylsulphoxyacetic Acid. II. RUDOLF PUMMERER (*Ber.*, 1910, **43**, 1401—1412. Compare Abstr., 1909, i, 580).—Phenylsulphoxyacetic acid is obtained by passing dry nitrous fumes into dry ethereal phenylthiolacetic acid; by the addition of petroleum, a brown oil separates, which evolves nitric oxide (?), and yields phenylsulphoxyacetic acid. *Phenylbenzylsulphoxide*, $CH_2Ph\cdot SOPh$, m. p. 125·5°, obtained in a similar manner from phenyl benzyl sulphide, does not yield thiophenol by heating with 50% sulphuric acid, and forms benzyl chloride and a little benzaldehyde with alcoholic hydrogen chloride. The preceding sulphoxides are also very conveniently prepared by the oxidation of phenylthiolacetic acid and phenyl benzyl sulphide by 33% hydrogen peroxide in glacial acetic acid. Diethyl sulphide is converted by this oxidising agent, with careful cooling, into diethyl sulphoxide, which forms with a solution of hydroferrocyanic acid, a stable, crystalline *hydroferrocyanide*, $C_4H_{10}OS,H_4Fe(CN)_6,H_2O$, which turns blue at 140°.

Phenylthiolacetic acid is converted by alcoholic hydrogen chloride into the ethyl *ester*, b. p. 144—145°/14 mm., an ethereal solution of which yields with sodium a yellowish-white, powdery sodio-derivative, which reacts with ethereal methyl iodide to form *ethyl α-phenylthiolpropionate*, $SPh\cdot CHMe\cdot CO_2Et$, b. p. 139·5°/14·5—15 mm., an ethereal solution of which also reacts with sodium.

α-Phenylthiolpropionic acid, obtained from α-bromopropionic acid and thiophenol in alkaline solution, is converted by cold hydrogen peroxide in glacial acetic acid into *α-phenylsulphoxypropionic acid*, $Ph\cdot SO\cdot CHMe\cdot CO_2H$, m. p. 135°, which is converted into thiophenol and pyruvic acid by boiling 25% sulphuric acid. The oxidation of ethyl phenylthiolacetate by 33% hydrogen peroxide and glacial acetic acid at 40—50° leads to the formation of *ethyl phenylsulphoxyacetate*, b. p. 152—154°/3 mm., a colourless, almost odourless, mobile liquid, which decomposes at 220—230°, yielding thiophenol and ethyl phenylthiolacetate and other products, is decomposed by cold fuming hydrochloric acid with the formation of thiophenol, and is easily hydrolysed by alcoholic potassium hydroxide, which, even when boiling, does not cause the generation of thiophenol.

A migration of oxygen from sulphur to carbon occurs when ethyl phenylsulphoxyacetate is heated with acetic anhydride, whereby *ethyl α-acetoxyphenylthiolacetate*, $SPh\cdot CH(OAc)\cdot CO_2Et$, b. p. 172·5°/15 mm., is formed. *Phenylthiolmethyl acetate*, $SPh\cdot CH_2\cdot O\cdot COMe$, b. p. 249°/713 mm., is obtained by heating phenylsulphoxyacetic acid with acetic anhydride, or, better, by the action of lead peroxide on phenylthiolacetic acid in boiling glacial acetic acid; it yields thiophenol very readily by treatment with alcoholic potassium hydroxide. C. S.

Distyrene. CARL LIEBERMANN (*Ber.*, 1900, **43**, 1543—1544).—The author agrees with Erlenmeyer (this vol., i, 309) that the compound described previously (Abstr., 1889, 1196) as distyrene is stilbene. J. J. S.

Triarylmethyls. IV. WILHELM SCHLENK, ANNA HERZENSTEIN, and TOBIAS WEICKEL (*Ber.*, 1910, **43**, 1753—1758. Compare Abstr., 1909, i, 791; this vol., i, 236, 237).—Gomberg and Cone (Abstr., 1906, i, 414, 821) by the action of silver on ω-chlorophenyldiphenylenemethane in presence of air obtained phenyldiphenylenemethyl peroxide; in the absence of air a hydrocarbon was formed, which they could not isolate. When ω-chlorophenyldiphenylenemethane is heated in benzene with copper bronze or copper powder in an atmosphere of carbon dioxide, *diphenylbisdiphenylene-ethane*, $\begin{array}{c}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CPh\cdot CPh<\!\!\begin{array}{c}C_6H_4\\ |\\ C_6H_4\end{array}$, is formed. This crystallises in long, obliquely-cut plates, m. p. 205—230° (decomp.), or when heated in sealed tubes in an atmosphere of carbon dioxide, m. p. 254°.

Solutions in organic solvents become more or less brown in colour on heating, the colour vanishing again on cooling. This change is attributed to dissociation into the methyl compound, $\cdot CPh<\!\!\begin{array}{c}C_6H_4\\ |\\ C_6H_4\end{array}$; it is specially marked in anisole. The colourless solutions do not decolorise iodine solutions; the hot brown solutions rapidly decompose iodine solutions. Bisdiphenylbisdiphenylene-ethane (*loc. cit.*, 238) hardly shows any tendency to dissociate.

Phenylbisdiphenylmethyl, $CPh(C_6H_4\cdot C_6H_5)_2$, is now obtained as a colourless powder. This is only slowly soluble in benzene; the solution is at first colourless and then red. Molecular-weight determinations indicate that 80% of the compound is present as methyl derivative. E. F. A.

***s*-Dichlorotetraphenylethane.** HANS FINKELSTEIN (*Ber.*, 1910, **43**, 1533—1535. Compare Schmidlin and von Escher, this vol., i, 369).—*s*-Dichlorotetraphenylethane can be prepared by the action of sodium iodide on an acetone solution of ω-dichlorodiphenylmethane. If a large excess of the iodide is used, tetraphenylethylene is formed, but with a mixture of two parts of the chloro-derivative, 1·4 of sodium iodide, and 10 of acetone, a 75% yield of the dichlorotetraphenylethane can be obtained by keeping at the ordinary temperature for two days. The same product is formed by the addition of chlorine to tetraphenylethylene, although the unsaturated hydrocarbon does not combine with bromine. When heated alone or with indifferent solvents of high boiling point, hydrogen chloride is formed, together with impure tetraphenylethylene. The unsaturated hydrocarbon contains chlorine attached to one of the benzene nuclei.

When the dichloro-derivative is boiled with methyl alcohol, the chief product is β-benzopinacoline. J. J. S.

Preparation of Acylaminophenylsulphonamic Acids. HUGO WEIL and KARL WEISSE (D.R.-P. 221301).—Acylaminophenyl

sulphonamic acids and their homologues are readily prepared by heating acylnitroanilines with an aqueous solution of sodium hydrogen sulphite. By the action of halogens in aqueous alkaline solution on these compounds, substituted halogen derivatives are formed; from these the acyl and sulpho-groups are removed by heating with mineral acid and subsequent boiling with alkali hydroxide, yielding halogenated diamines.

If boiled with alkali, the acyl gronp only is removed, and on acidification the crystalline *anilinesulphonamic acid* is precipitated; this is readily diazotised, yielding *diazobenzenesulphonamic acid*, which by contact with dilute mineral acid is converted into diazo-*p*-aminobenzene. F. M. G. M.

Trinitro-*p*-anisidine. FRÉDÉRIC REVERDIN [with A. DE LUC] (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 476—483; *Compt. rend.*, 1910, **150**, 1433—1435*).—When benzoyl-2 : 3-dinitro-*p*-anisidine (Abstr., 1909, i, 377) is nitrated with nitric acid (D 1·52), first at 5—10°, and then at 60° for five minutes, *nitrobenzoyl-*2 : 3 : 6-*trinitro*-p-*anisidine* is obtained as a felted mass of colourless, slender needles, m. p. 247°. When treated with three times its weight of strong sulphuric acid on the water-bath, it gives on cooling a brilliant red precipitate of the corresponding 2 : 3 : 6-*trinitro*-p-*anisidine*, m. p. 127—128°. From aqueous solutions large, reddish, orthorhombic crystals are obtained [$a:b:c = 0·738287 : 1 : 0·812027$]. The action of acetic anhydride in the presence of a small quantity of concentrated sulphuric acid gives the *acetyl* derivative, $C_9H_8O_8N_4$; white needles, m. p. 242°.

One of the nitro-groups (it is not certain which) in trinitro-*p*-anisidine is very reactive. When heated with excess of various bases, compounds of the general formula $OMe·C_6H(NO_2)_2R·NH_2$ are produced, R representing the residue of the base employed. The *aniline* derivative, $C_{13}H_{12}O_5N_4$, has m. p. 148°, and forms brown spangles; the p-*toluidine* derivative, $C_{14}H_{14}O_5N_4$, forms brown, prismatic crystals, m. p. 139°; the *monomethylamine* derivative, $C_8H_{10}O_5N_4$, crystallises in reddish-violet needles, m. p. 199—200°.

When trinitro-*p*-anisidine is heated in alcoholic solution with sodium acetate, a reddish-brown precipitate of the sodium salt of a *dinitrohydroxy*-p-*anisidine*, $OMe·C_6H(NO_2)_2(OH)·NH_2$, is obtained. On the addition of acid to the aqueous solution of this salt, brown needles of the dinitrohydroxy-*p*-anisidine are obtained, m. p. 161°. The *acetyl* derivative is obtained by treatment with acetic anhydride and concentrated sulphuric acid; small, white needles, m. p. 193—194°.

In the nitration of benzoyl-2 : 3-dinitro-*p*-anisidine another product is formed besides nitrobenzyl-2 : 3 : 6-trinitro-*p*-anisidine. It forms pale yellow needles, and has m. p. 259°. Analysis points to the formula $C_{14}H_{10}O_8N_4$, and it is either a benzoyltrinitroanisidine or a nitrobenzoyldinitroanisidine. T. S. P.

Amines. III. Alkylations with Dimethyl Sulphate. Synthesis of Dimethylphenylethylamine. TREAT B. JOHNSON and HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1910, **32**, 761—770).—It has been shown previously (Abstr., 1909, i, 785) that methyl iodide reacts with phenylethylamine to form the hydriodide of the original base

* and *Ber.*, 1910, **43**, 1849—1853.

and phenylethyltrimethylammonium iodide, but that the mono- and di-methyl derivatives are not produced. It has now been found that phenylethyldimethylamine, $CH_2Ph \cdot CH_2 \cdot NMe_2$, can be prepared by the action of methyl sulphate on phenylethylamine in presence of sodium methoxide. This amine has been obtained in small quantity by Barger (Trans., 1909, **95**, 2195) by heating phenylethyl chloride with dimethylamine. When *p*-nitrophenylethylamine (Johnson and Guest, this vol., i, 311) is treated with methyl sulphate, alkylation does not take place, but the amine remains unchanged. Attempts have also been made to prepare secondary and tertiary amines from *p*-nitrophenylethylamine by alkylation with methyl iodide, but without success.

When methyl sulphate is heated with an ethereal solution of phenylethylamine, *phenylethylammonium methyl sulphate*,

$$CH_2Ph \cdot CH_2 \cdot NH_3 \cdot SO_4 \cdot Me,$$

m. p. 75—77°, is obtained in the form of lustrous plates, together with a hygroscopic quaternary *salt*, m. p. 100—110° (decomp.).

Phenylethyldimethylamine, b. p. 200—205°, is a strong base, and absorbs carbon dioxide from the air. The *platinichloride* decomposes at 221°; the *hydrochloride* has m. p. 205°.

When phenylethylmethylamine (Johnson and Guest, *loc. cit.*) is heated with thioacetic acid, *acetyl*-p-*nitrophenylethylmethylamine*, $CH_2Ph \cdot CH_2 \cdot NMeAc$, is obtained as a dark-coloured oil, and, on nitration, yields the p-*nitro*-derivative, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMeAc$, m. p. 100—101°, which, on oxidation with potassium dichromate, furnishes *p*-nitrobenzoic acid. When acetyl-*p*-nitrophenylethylmethylamine is digested with hydrobromic acid, it is converted into p-*nitrophenylethylmethylamine hydrobromide*; the base was obtained as a heavy, yellow oil. By the action of phenylthiocarbimide on *p*-nitrophenylethylmethylamine, *α-phenyl-β*-p-*nitrophenylethyl-β-methylthiocarbamide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe \cdot CS \cdot NHPh$, m. p. 137—138°, is produced, which crystallises in plates.

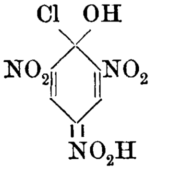
By reducing *p*-nitrophenylethylamine with tin and hydrochloric acid, *p*-aminophenylethylamine (Johnson and Guest, *loc. cit.*) is produced. When *p*-nitrophenylethylamine is heated with methyl iodide, the hydriodide of the amine is obtained, together with p-*nitrophenylethyltrimethylammonium iodide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_3I$, m. p. 200—201°, which forms hexagonal prisms. E. G.

Solubility Equilibrium between Phenanthrene and 2:4-Dinitrophenol. ROBERT KREMANN and F. HOFMEIER (*Monatsh.*, 1910, **31**, 201—202).—Phenanthrene forms additive compounds with trinitrobenzene and trinitrotoluene, but not with the dinitro-compounds (Abstr., 1905, i, 77; 1909, i, 29).

An examination of the freezing-point curve of mixtures of phenanthrene and 2:4-dinitrophenol proves that these compounds do not form a definite compound; the curve has only one eutectic point, namely, at 61°. J. J. S.

Picric Acid. A. STEPANOFF (*Annalen*, 1910, **373**, 219—226).—The solubility of picric acid in water is decreased at first by the addition of hydrogen chloride, but reaches a minimum when the solution contains roughly 0·5 millimol. of picric acid and 150 millimols.

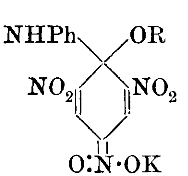
of hydrogen chloride in 100 c.c. of the solution, after which the solubility increases as the concentration of hydrogen chloride becomes greater. It seems probable, therefore, that picric acid and hydrogen chloride combine, forming an unstable additive product having the annexed formula, the proportion of which capable of existing in solution will depend on the concentration of the hydrogen chloride. If the quantity of hydrogen chloride is insufficient, the additive compound will decompose, yielding the true trinitrophenol rather than the *aci*-form, since not only do quinonoid compounds tend to pass into benzenoid compounds, but the true trinitrophenol is less soluble than the coloured *aci*-form.



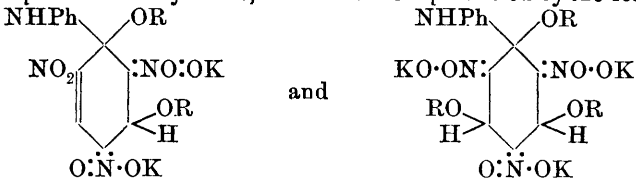
The dark modification of picric acid described by Georgievics (compare Abstr., 1906, i, 420) is shown to be ammonium picrate, formed by the absorption of ammonia from the air. W. H. G.

Colour of Ammonium Picrate. A. STEPANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 495—497).—By rapid crystallisation of an almost saturated solution, or by the action of gaseous ammonia on picric acid, a bright yellow ammonium picrate is obtained, the crystals being much smaller than those of the brownish-yellow variety, which is obtained on slower crystallisation; both modifications give a bright yellow powder (compare Silberrad and Phillips, Trans., 1908, **93**, 474). These two forms can be deposited in one and the same vessel by varying the rate of cooling, and show no sign of changing, one into the other, when left in this vessel for some months. Heating for some hours at 100° is likewise unaccompanied by interconversion of the two forms. At 170—180° part of the picrate volatilises, the crystals becoming corroded and assuming a yellow colour. The solutions of the two modifications are identical. The magnitude of the crystals is without influence on their colour, but in the powdered state the red and yellow forms are optically identical. Under the microscope, fragments of the crystals retain their transparency (compare Hantzsch, Abstr., 1906, i, 352, 353; 1907, i, 207, 500; Dimroth and Dienstbach, Abstr., 1909, i, 62; Korczyński, Abstr., 1909, i, 148). T. H. P.

Salts of Aromatic Polynitro-compounds. MAX BUSCH and WALTER KÖGEL (*Ber.*, 1910, **43**, 1549—1564. Compare Sudborough and Picton, Trans., 1906, **89**, 593; Busch and Pungs, Abstr., 1909, i, 564).—The salts formed from compounds of the type of picrylaniline are not simple compounds: $C_6H_2(NO_2)_3{\cdot}NKPh$, but are formed by the addition of potassium alkyloxide to the nitro-compound, and are represented by quinonoid formulæ, for example, the annexed constitution. Compounds of the type of picrylmethylaniline also yield similar salts, the only exception being picrylmethyl-α-naphthylamine, which appears to be incapable of forming salts. Picryl α-naphthylamine forms a potassium salt which does not contain alcohol (compare Sudborough and Picton, *loc. cit.*).



The nitro-compounds can also form salts containing 2 or even 3 mols. of potassium alkyloxide, and these are represented by the formulæ:



The di-potassium compounds, as a rule, have not such a deep red colour as the mono-potassium salts, and the tri-potassium salts, which have a hexamethylene constitution, are pale yellow in colour.

Picrylaniline potassium methoxide (*potassium* 3 : 5-*dinitro*-4-*anilino*-4-*methoxyquinolnitrosate*), $C_{13}H_{11}O_7N_4K$, crystallises in glistening, black plates with a steel-blue lustre. It loses a molecule of methyl alcohol when heated at 111°, melts at 115—120°, and explodes at higher temperatures. The corresponding *ethyl* compound has m. p. 115°.

Picrylaniline dipotassium ethoxide, $C_{16}H_{18}O_8N_4K_2$, forms dark red crystals with no definite m. p., and the *tripotassium ethoxide*,

$$C_{18}H_{23}O_9N_4K_3,$$

forms a yellow, microcrystalline powder, which turns red when washed with alcohol.

Picrylaniline potassium propoxide, bluish-black plates, and the corresponding *tripotassium* compound have been prepared. With potassium hydroxide in *iso*butyl alcoholic solution, only the *tripotassium* salt, $C_{24}H_{35}O_9N_4K_3$, could be obtained as an orange-yellow precipitate.

Picrylmethylaniline tripotassium ethoxide is a reddish-brown amorphous powder. *Picrylmethylaniline dipotassium propyloxide*, $C_{19}H_{24}O_8N_4K_2$, is similar.

Picryl-β-naphthylamine potassium methoxide, $C_{17}H_{13}O_7N_4K$, forms black needles, m. p. 173°, and is hydrolysed by water. The corresponding *ethoxide*, $C_{18}H_{15}O_7N_4K$, has m. p. 168°, and the *dipotassium* iso*butyloxide*, $C_{20}H_{18}O_7N_4K_2$, is a pale red, amorphous compound.

Picryl-α-naphthylamine is oxidised in alcoholic solution by an *N*-solution of silver nitrate to an orange-coloured, crystalline *compound*, $C_{16}H_{10}O_7N_4$, m. p. 296—297°.

Picryl chloride and methyl-α-naphthylamine yield an additive *compound*, $C_{17}H_{11}O_6N_4Cl$, in the form of dark red, felted needles, m. p. 94°.

Dibenzylpicramide, $C_{20}H_{16}O_6N_4$, crystallises in yellow needles, m. p. 173°, and yields a potassium salt.

2 : 4-*Dinitrodiphenylamine potassium methoxide*, $C_{13}H_{12}O_5N_3K$, crystallises in violet-black, glistening needles, and the *potassium* iso*butyloxide*, $C_{16}H_{18}O_5N_3K$, is similar.

The alkyl derivatives of 2 : 4-dinitrodiphenylamine, for example,

$$C_6H_3(NO_2)_2\cdot NEtPh,$$

do not yield potassium salts, neither does dimethyl-2 : 4-dinitroaniline. Methyl-2 : 4-dinitroaniline yields an unstable, dark red *potassium* salt,

s-Trinitrobenzene yields a definite *compound* with 3 molecules of potassium propyloxide, $C_{15}H_{24}O_9N_3K_3$, which forms a red powder. *s*-Trinitrotoluene behaves in a similar manner. J. J. S.

Homochromoisomerism. ARTHUR HANTZSCH (*Ber.*, 1910, **43**, 1651—1662).—Chromoisomerides are substances which are chemically identical, but optically dissimilar, exhibiting differences in colour and absorption. The author describes a new kind of isomerism called homochromoisomerism. Homochromoisomerides are identical, not only chemically, but also optically, possessing the same colour, absorption, molecular extinction, and molecular refraction, but differ in m. p., solubility, etc. The only instances so far obtained are those of quinoneoximes and nitrated anilines.

[With JOSEPH LISTER.]—Picrylphenylmethylamine,

$$C_6H_2(NO_2)_3\cdot NMePh,$$

exists in two forms, each of which is unimolecular. The α-form, m. p. 108—110°, has been obtained by Turpin (Trans., 1891, **59**, 716), and crystallises unchanged in dark red prisms from methyl or ethyl alcohol, acetic acid, ethyl acetate, ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, and pyridine. The β-form, m. p. 128—129° (Sudborough and Picton, Trans., 1906, **89**, 83), crystallises unchanged from benzene, acetonitrile, pyridine, or carbon disulphide. The α-form is converted into the β at 100° or by crystallisation from benzene. The β-form is changed into the α by crystallisation from methyl alcohol, ether, acetone, ethyl acetate, carbon tetrachloride, or chloroform. Both forms have identical absorption spectra, and practically identical molecular extinctions and molecular refractions (in pyridine).

o-Tolyl-2 : 4-dinitroaniline exists in two orange forms (and also in two yellow forms: compare following abstract), which are homochromoisomerides having the same absorption spectra, molecular extinctions, and molecular refractions.

[With R. FLADE.]—The *syn*- and the *anti*-modifications of quinoneoximes and also their salts are homochromoisomerides. The two forms of Kehrmann's chlorotoluquinoneoxime have the same absorption spectra and molecular extinctions; the alcoholic solutions of their potassium salts have the same molecular extinctions, and aqueous solutions of the cæsium salts have the same molecular refractions.

[With CURT B. HARTUNG.]—The preceding instance of homochromoisomerism has led to a more searching examination of the optical behaviour of other stereoisomeric oximes. *syn*- and *anti*-Benzilmonoximes are both colourless, and form yellow alkali salts, but their absorption spectra and molecular extinctions are different. The same is true of the stereoisomeric *p*-nitrobenzaldoximes.

The difference in the optical behaviour of the *syn*- and the *anti*-modifications of benzilmonoxime and also of *p*-nitrobenzaldoxime is probably due to the fact that the oximic hydroxyl is further removed from the unsaturated carbonyl or nitro-group in the *anti*- than in the *syn*-form; in the quinoneoximes the distance is the same in both modifications, $O{:}C_6H_2MeCl{:}\underset{OH}{N}$ and $O{:}C_6H_2MeCl{:}\overset{OH}{\dot{N}}$, and therefore the

groups exert the same chemical and optical influence in both cases.

Homochromoisomerism, therefore, may represent an extreme case of stereoisomerism in which the mutual influence of unsaturated groups is not markedly affected by differences of configuration. C. S.

Chromoisomerism and Homochromoisomerism of Nitroanilines. ARTHUR HANTZSCH (*Ber.*, 1910, **43**, 1662—1685).—A large number of nitrated anilines have been examined for the existence of differently coloured isomerides (chromoisomerides) or of similarly coloured isomerides (homochromoisomerides). Examples of the latter have been found only in picrophenylmethylamide and in *o*-tolyl-2 : 4-dinitroaniline (preceding abstract), but instances of chromoisomerides are quite numerous in mono-, di-, and tri-nitroanilines containing mono- or di-substituted amino-groups.

The author develops his views at some length in a manner unsuitable for abstraction, and arrives at the following conclusions.

Nitrated anilines can exist in yellow, orange, and dark red forms; occasionally also in modifications having the same colour but different m. p. All these forms are unimolecular in solution. In one and the same solvent isomeric nitroanilines are optically identical, exhibiting the same absorption spectra, molecular refractions, and extinctions. Chromoisomeric nitroanilines contain chromophores of different constitution, whilst the constitutions of homochromoisomerides are explained on stereochemical grounds (preceding abstract). C. S.

Peculiar Change Caused by Heating Salts of Phenolsulphonic Acids. JULIUS OBERMILLER (*Ber.*, 1910, **43**, 1413—1420).—The melting of potassium *o*- and *p*-phenolsulphonates at 255—260° and 325—330° respectively are not cases of true fusion, but are caused by the decomposition of the salts with liberation of phenol. Thus potassium *o*-phenolsulphonate, when heated at a temperature not exceeding 300°, gives off about one-half of its phenol, and leaves an infusible residue consisting of potassium phenol-2 : 4-disulphonate containing a little phenol-2 : 4 : 6-trisulphonate. Other salts, such as the sodium, magnesium, and barium salts, which are infusible, behave in a similar way, only more slowly and at a higher temperature. C. S.

Structural Conditions Determining Anomalies in Boiling Points Among *o*-Substituted Phenols. C. GUILLAUMIN (*Bull. Soc. chim.*, 1910, [iv], **7**, 426—431).—It is known that phenols containing the group –CHO or –CO·OR in the ortho-position to the hydroxyl show anomalous boiling points; thus, *o*-hydroxybenzaldehyde, b. p. 196°, might be expected to boil at 245° (approx.), and methyl salicylate has b. p. 224°, instead of the expected value, 260°. Similar anomalous boiling points are shown by phenols containing the ψ-allyl side-chain in the ortho-position.

The author correlates these anomalies with (1) the presence of a free hydroxyl group, (2) the existence of an ortho-substituent possessing a double linking to the cyclic atom (carbon or nitrogen). It is possible

that such substances may at the point of ebullition pass into tautomeric forms of lower boiling point, and possible formulæ for these are suggested; thus ψ-allyl-*o*-phenol might be represented by one of the following formulæ:

$$C_6H_5{<}\begin{matrix}O\text{———}\\CMe\end{matrix}{>}CH_2 \qquad C_6H_4{<}\begin{matrix}O\text{———}\\CHMe\end{matrix}{>}CH_2 \quad \text{or} \quad OH\cdot C_6H_4{<}\begin{matrix}CH_2\\ |\\ CMe\end{matrix}.$$

(I.) (II.) (III.)

No. II has a coumaran nucleus, and probably represents too stable a structure for this pnrpose. No. I would explain the lowering of boiling points in these compounds, but No. III has the advantage of being more readily applicable to the other cases mentioned, such as salicylaldehyde, methyl salicylate, etc. T. A. H.

Dehydrodicarvacrol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1910, **150**, 1333—1336).—Dehydrodicarvacrol, $OH\cdot C_6H_2MePr^{\beta}\cdot C_6H_2MePr^{\beta}\cdot OH$, was obtained in an impure state by Dianine (Abstr., 1882, 623), and described under the name of β-thymol. It is best prepared as follows: Carvacrol (40 c.c.) is dissolved in 95% alcohol (400 c.c.), and poured into 100 litres of water. The liquid is shaken, filtered, and treated with 300 c.c. of ferric chloride solution (26%). After ten days the precipitate is collected, dissolved in alkali, reprecipitated by acetic acid, and crystallised from dilute alcohol, from which the compound separates ın long, silky needles, m. p. 165—166°, containing $2H_2O$.

Dehydrodicarvacrol gives no coloration with ferric chloride. The *dimethyl ether* crystallises in small prisms, m. p. 110°; the *diacetate* forms lamellæ or felted needles, m. p. 182—183°; the *dıbenzoate* occurs in long, prismatic needles, m. p. 185°. W. O. W.

Reduction with Metallic Calcium and Absolute Alcohol. CHARLES MARSCHALK and FANNY NICOLAJEWSKY (*Ber.*, 1910, **43**, 1700—1702. Compare this vol., i, 269).—By means of metallic calcium and absolute alcohol, benzoveratrole, veratroylveratrole, and veratroyl quinol dimethyl ether are reduced to the corresponding leuco-compounds. Tetramethyl-*p*-diaminobenzophenone forms tetramethyl-*p*-diaminobenzhydrol. Naphthalene and anthracene yield dihydro-compounds; quinoline yields tetrahydroquinoline and an amorphous product. Pyridine yields ammonia and small quantıties of a base with an odour like piperidine, indicating the opening of the ring; piperidine gives no ammonia. E. F. A.

***cyclo*Hexanetriols and their Derivatives.** LÉON BRUNEL (*Compt. rend.*, 1910, **150**, 986—988. Compare Abstr., 1905, i, 869).—When an ethereal solution of ethoxy-Δ^2-*cyclo*hexene is treated with iodine and mercuric oxide, an oily liquid is obtained having the composition $OEt\cdot C_6H_9I\cdot OH$, whilst if alcohol is used as the solvent, the composition of the product is represented by $C_6H_9I(OEt)_2$.

Potassium hydroxide converts the first-mentioned iodo-derivative into an *ether*, b. p. 90—91°/25 mm., which, when heated with water, furnishes *ethoxy*cyclo*hexane*-2 : 3-*diol*, $OEt\cdot C_6H_9(OH)_2$, b. p.

148—149°/20 mm. When this is hydrolysed by aqueous hydrobromic acid, a mixture of triols is obtained, which may be separated by fractional crystallisation of their acetates or benzoates.

a-cyclo*Hexane*-1 : 2 : 3-*triol*, $C_6H_9(OH)_3$, crystallises in needles, m. p. 108°; the *triacetate* forms prisms, m. p. 126° with sublimation; the *tribenzoate* occurs in long needles, m. p. 141—142°. *β*-cyclo*Hexane*-1 : 2 : 3-*triol*, m. p. 124°, forms a syrupy *triacetate* and a *tribenzoate* crystallising in large prisms, m. p. 181°. The *β*-compound is formed in larger proportion and free from the *a*-isomeride by oxidising ethoxy*cyclo*-Δ^2-hexane with alkaline permanganate and treating the product, *ethoxy*cyclo*hexane*-2 : 3-*diol*, with hydrobromic acid. W. O. W.

Phenols of the Type $OH\cdot C_6H_3Me\cdot CMe\colon CH_2$ with *ψ*-Allyl Side-chains. I. *ψ*-Allyl-*o*-cresol. II. *ψ*-Allyl-*m*-cresol. III. *ψ*-Allyl-*p*-cresol. C. Guillaumin (*Bull. Soc. chim.*, 1910, [iv], 7, 374—383).—The synthesis of the methyl ethers of these *ψ*-allyl phenols has been described already (Béhal and Tiffeneau, Abstr., 1908, i, 630, and this vol., i, 374; Guillaumin, this vol., i, 375). In this paper an account is given of the application of analogous methods to the preparation of the three isomeric phenols and their derivatives.

Methyl *o*-hydroxytoluate, D^0 1·1683, $D^{16\cdot8}$ 1·1529, $n_D^{16\cdot8}$ 1·53538, m. p. −0·5°, b. p. 237—239°/760 mm. or 119—121°/14 mm. (corr.), furnishes with magnesium methyl iodide (3·5 mols.) o-*hydroxytolyldimethylcarbinol*, $OH\cdot C_6H_3Me\cdot CMe_2\cdot OH$ [2 : 1 : 3], m. p. 75·5°, b. p. 140—144°/14 mm. (corr.), which forms colourless crystals from benzene, and when heated decomposes at 208—213°, yielding an unsaturated hydrocarbon; when heated with acetic anhydride during twelve hours it furnishes o-*acetoxy-ψ-allyltoluene*,

$$OAc\cdot C_6H_3Me\cdot CMe\colon CH_2$$

[2 : 1 : 3], D^0 1·0337, b. p. 236—238°/760 mm. or 115—116°/13 mm. (corr.), a colourless liquid, which gradually becomes green and decolorises bromine or potassium permanganate. On hydrolysis with potassium hydroxide in alcohol, this acetate furnishes *ψ*-allyl-*o*-cresol, $OH\cdot C_6H_3Me\cdot CMe_2\colon CH_2$ [2 : 1 : 3], D^0 1·0143, $D^{15\cdot6}$ 0·9980, $n_D^{15\cdot6}$ 1·54193 (compare Béhal and Tiffeneau, *loc. cit.*).

The following meta-isomerides of the above substances were prepared from methyl *m*-hydroxytoluate, D^0 1·1621, $D^{15\cdot2}$ 1·1483, $n_D^{15\cdot2}$ 1·53781, b. p. 242—244°/760 mm. (corr.) (compare Abstr., 1908, i, 630). *m*-Hydroxytolyldimethylcarbinol, m. p. 64°, b. p. 140—143°/14 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 824), with acetic anhydride yields the corresponding m-*acetoxy-ψ-allyltoluene*, D^0 1·0358 $D^{13\cdot8}$ 1·0238, $n_D^{13\cdot8}$ 1·51790, b. p. 122—123°/764 mm. (corr.), a colourless liquid which becomes lemon-yellow after several days. On hydrolysis this acetate yields *ψ*-allyl-*m*-cresol, D^0 1·0241, $D^{14\cdot6}$ 1·0130, $n_D^{14\cdot6}$ 1·55329, b. p. 221—222°/758 mm. or 106—107°/13 mm. (corr.), a colourless liquid giving a green coloration with ferric chloride (compare Fries and Fickewirth, Abstr., 1908, i, 160). It condenses with chloroacetic acid, forming *ψ-allyl*-m-*tolyloxyacetic acid*, m. p. 112°, which crystallises from aqueous alcohol in colourless needles, and polymerises rapidly on distillation at atmospheric pressure.

The following para-isomerides were prepared in like manner from

methyl *p*-hydroxytoluate, D^{0} 1·1673, $D^{15·8}$ 1·1534, $n_D^{15·8}$ 1·53514, m. p. − 1°, b. p. 241—243°/767 mm. or 122—124°/14 mm. (corr.): *p*-Hydroxytolyldimethylcarbinol, m. p. 81°, b. p. 144—148°/14 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 824). p-*Acetoxy-ψ-allyltoluene*, D^{0} 1·0383, b. p. 244—246°/763 mm. or 129·5—131·5°/13 mm. (corr.), is a colourless liquid, which becomes orange-red after a few hours. *ψ*-Allyl-*p*-cresol, D^{0} 1·0285, $D^{15·5}$ 1·0177, $n_D^{15·5}$ 1·54987, b. p. 220—222°/760 mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 160). When condensed with chloroacetic acid, it furnishes *ψ-allyl*-p-*tolyloxyacetic acid*, $CO_2H·CH_2·O·C_6H_3Me·CMe{:}CH_2$ [2 : 5 : 1], m. p. 97°, which crystallises in long, colourless needles from boiling alcohol, and is slightly soluble in cold, more so in hot water, and very soluble in ether.

The author was unable to obtain the crystalline polymerides of *ψ*-allyl-*m*-cresol and of its *p*-isomeride described by Fries and Fickewirth (*loc. cit.*). T. A. H.

Phenylic Transposition of ψ-Allyl Phenyl Ethers Derived from *o*- or *p*-Cresol. C. GUILLAUMIN (*Bull. Soc. chim.*, 1910, [iv], 7, 420—426).—It has been shown previously that the iodohydrins of aromatic compounds containing *ψ*-allyl side-chains, when treated with silver nitrate or yellow mercuric oxide, are transformed into derivatives of acetone, thus: $Ar·CMe(OH)·CH_2I \longrightarrow Ar·CH_2·COMe$ (Tiffeneau, Abstr., 1907, i, 304; 1908, i, 165, 166). It is now shown that a like transposition is brought about by the action of moist silver oxide on the iodohydrin, but that in this case the iodine atom is, in part, normally replaced by an −OH group, giving rise to the corresponding glycol, thus: $Ar·CMe(OH)·CH_2I \longrightarrow Ar·CMe(OH)·CH_2·OH$. The substances studied so far indicate (1) that "steric hindrance" plays no part in preventing the transposition of the aromatic radicle in the first action, and (2) that in the transposed aromatic radicle no change in the positions of substitution occurs.

2-Methoxy-1-methyl-3-*ψ*-allylbenzene (this vol., i, 375), on treatment with iodine and yellow mercuric oxide in ether, gives an iodohydrin, which with silver nitrate furnishes 2-*methoxy*-1-*methyl*-3-*acetonylbenzene*, D^{0} 1·0571, b. p. 257—259°/763 mm. (corr.); the sodium hydrogen sulphite compound of this is readily dissociated by water; the *semicarbazone*, recrystallised from benzene, separates into two fractions, m. p. 169° and 171° respectively. With moist silver oxide the iodohydrin yields the same ketone, and in addition the *glycol*,

$$OMe·C_6H_3Me·CMe(OH)·CH_2·OH \ [2:1:3],$$

b. p. 200—220°/13 mm., D^{0} 1·1100, a viscous liquid, which on distillation at atmospheric pressure furnishes the corresponding *aldehyde*, $OMe·C_6H_3Me·CHMe·CHO$ [2 : 1 : 3].

4-Methoxy-1-methyl-3-*ψ*-allylbenzene furnishes an iodohydrin, which on treatment with silver nitrate yields 4-*methoxy*-1-*methyl*-3-*acetonylbenzene*, b. p. 266—267°/75 mm. (corr.), D^{0} 1·0583, $D^{14·8}$ 1·0460, $n_D^{14·8}$ 1·52324, a colourless liquid, which combines with sodium hydrogen sulphite only when pure, and in concentrated solution in ether; the *semicarbazone*, m. p. 150°, crystallises from benzene. T. A. H.

Conversion of Hydroaromatic Alcohols into the Corresponding Phenols. Léon Brunel (*Compt. rend.*, 1910, **150**, 1528—1530).—To ascertain whether the side-chain undergoes any change during the direct hydrogenation of thymol by the method already described (Abstr., 1905, i, 197), the author has oxidised the product, thymomenthol, with chromic acid, and brominated the thymomenthone so formed. *Dibromothymomenthone*, $C_{10}H_{16}OBr_2$, crystallises in large prisms, m. p. 97°, and on heating with quinoline furnishes thymol identical with the starting material. Thymol was also formed on submitting menthol or thymomenthol to catalytic dehydrogenation in presence of reduced copper at 230—240°. Under the same conditions, carvomenthol (Abstr., 1906, i, 81) was converted into carvacrol, an unsaturated *hydrocarbon*, $C_{10}H_{18}$, b. p. 174—176°, being formed as a by-product. The corresponding *hydrocarbon* from menthol or thymomenthol had b. p. 166—168°. W. O. W.

Simple Formation of Benzyl Ethers. Julius von Braun (*Ber.*, 1910, **43**, 1350—1352).—Compounds such as benzyl bromide and *o*-xylyl bromide, when boiled with dilute sulphuric acid and alcohol, or even with dilute alcohol, have the bromine replaced by the alkyloxy-group, and ethers are formed.

In this way the following have been prepared : Benzyl methyl ether, b. p. 174° (previously given as 167—171°); benzyl ethyl ether, b. p. 189° (previously given as 185—186°); *o-xylyl ethyl ether*, b. p. 208—210°, which has an odour like peppermint; *benzyl allyl ether*, b. p. 204—205°, which has a pleasant ethereal odour; at the same time a compound, which is not volatile in steam, b. p. 150—152°/9 mm., is obtained.

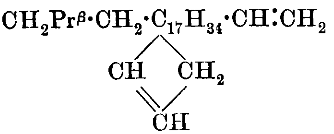
Benzyl bromide also reacts with glycol and glycerol, but a mixture of products is formed. Phenylethyl bromide does not react with alcohol in this manner. E. F. A.

Aminoaryl Alcohols. II. Formation of a Phenylglycol from the Ammonium Base of α-Amino-α-phenyl*iso*propyl Alcohol. Hermann Emde and Ernst Runne (*Ber.*, 1910, **43**, 1727—1729. Compare Abstr., 1909, i, 300).—The quaternary ammonium base derived from α-amino-α-phenyl*iso*propyl alcohol when warmed in aqueous solution is decomposed into trimethylamine and the β-form of α-phenylpropylene αβ-glycol (compare Zincke, Abstr., 1884, 1003; Zincke and Zahn, this vol., i, 316). The quaternary base contains two asymmetric carbon atoms, but fractional crystallisation of the following salts did not lead to any separation of the isomerides.

The *iodide*, $NMe_3I\cdot CHPh\cdot CHMe\cdot OH$, forms hard, short crystals, m. p. 176—177°. The *chloride*, $+H_2O$, crystallises in transparent, long plates, m. p. 138—139°, or when anhydrous, m. p. 196—197°. The *platinichloride* crystallises well, decomp. 233—234°; the *aurichloride* forms long, single needles, m. p. 151·5°, decomp. 220°. E. F. A.

Derivatives of Cholesterol. Leo Tschugaeff and W. Fomin (*Compt. rend.*, 1910, **150**, 1435—1437. Compare this vol., i, 31).—Cholesterylene, previously obtained by the decomposition of methyl

cholesterylxanthate, has now been separated by crystallisation from ether and alcohol into two isomeric hydrocarbons: *a-cholesterylene*, crystallising in needles, m. p. 77°, $[\alpha]_D$ $-109{\cdot}3°$ in toluene, and *β-cholesterylene*, m. p. 59°, $[\alpha]_D$ $-76{\cdot}68°$, in toluene solution. Both compounds show normal rotatory dispersion. When treated with hydrogen in presence of platinum-black, they yield the same hydrocarbon, cholestane, identical with that obtained from cholestene by Mauthner (Abstr., 1909, i, 714).



The annexed constitution is suggested for cholesterylene, the two modifications being supposed to differ in the position of the double linking in the ring. W. O. W.

Interchange of Alkyl Groups in Esters of Organic Acids. MICHAEL PFANNL (*Monatsh.*, 1910, 31, 301—317).—It has long been known that the alkyl group of an ester can be exchanged for another alkyl group by means of sodium or an alkali hydroxide dissolved in the alcohol corresponding with the second alkyl group. By means of experiments on the methyl, ethyl, and propyl esters of terephthalic acid, of benzoic acid, and of oxalic acid, the author shows that the exchange is quite general, and is completely reversible. The method consists in dissolving a known quantity of an ester in at least ten times the amount of an alcohol, and adding in the cold a quantity of potassium hydroxide or of sodium dissolved in the alcohol in question; the exchange proceeds to completion at the ordinary temperature in a time, thirty minutes to fifteen hours, depending on the amount of alkali present, the greater the amount of alkali the shorter the time required; the alkali is then neutralised, water is added, and the new ester is removed by ether or by filtration.

The velocity of the exchange is directly proportional to the quantity of alkali present; consequently Kremann's theory that the alkali acts merely as a catalyst (Abstr., 1908, i, 120) must be incorrect. The author regards Claisen's explanation:

$$CPh{\lessdot}^{O}_{OR} + KOR' = CPh{\lessdot}\begin{matrix}OR'\\OK\\OR\end{matrix} \longrightarrow CPh{\lessdot}^{OR'}_{O} + KOR$$

as affording the best interpretation of the results, for it explains (i) the reversibility of the exchange, (ii) the absence of any exchange in the absence of alkali, (iii) the absence of any exchange in the case of substances, such as phenolic ethers, which are unable to add on potassium alkyl oxide, (iv) the proportionality between the velocity of the exchange and the concentration of the alkali. C. S.

***cyclo*Hexylglycollic Acid.** MARCEL GODCHOT and JULES FREZOULS (*Compt. rend.*, 1910, 150, 1248—1250. Compare Zelinsky and Schwedoff, Abstr., 1908, i, 864).—*cyclo*Hexylglycollonitrile undergoes decomposition when distilled; hydrochloric acid converts it into the *amide*, crystallising in pearly leaflets, m. p. 155°. The free acid obtained by the hydrolysis of the amide with alkalis occurs as

prismatic needles, m. p. 130—131°; the *sodium* and *silver* salts have been analysed. In the authors' opinion, the acid described under this name by Zelinsky and Schwedoff was a mixture. W. O. W.

[Preparation of Isomeric Nitrobenzoyl Derivatives of Nitroanilines, Nitrotoluidines, and their Reduction Products.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 221433).—An account of the preparation of dyes from tetrazotised compounds of the general formula $NH_2\cdot R\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2$ (R = an aromatic nucleus) combined with two molecules of various naphtholsulphonic acids.

The following initial compounds are mentioned, and were prepared by the usual methods: m-*Nitrobenzoyl*-p-*nitroaniline*, yellow powder, m. p. 249°. m-*Aminobenzoyl*-p-*phenylenediamine*, brown needles, m. p. 150°. p-*Nitrobenzoyl*-p-*nitroaniline*, yellow, crystalline powder, m. p. 266°. p-*Aminobenzoyl*-p-*phenylenediamine*, brown needles, m. p. 205°, soluble in hot water. m-*Nitrobenzoyl*-m-*nitroaniline*, brown needles, m. p. 185°. m-*Aminobenzoyl*-m-*phenylenediamine*, m. p. 130°. p-*Nitrobenzoyl*-m-*nitroaniline*, yellow needles, m. p. 227°. p-*Aminobenzoyl*-m-*phenylenediamine*, grey powder, m. p. 173°. m-*Nitrobenzoyl*-p-*nitro*-o-*toluidine*, colourless, glistening leaflets, m. p. 193°. m-*Aminobenzoyl*-m-*tolylenediamine*, brown, crystalline powder, m. p. 177°. p-*Nitrobenzoyl*-p-*nitro*-o-*toluidine*, brownish-yellow needles, m. p. 214°.

F. M. G. M.

Bromination of Anthranilic Acid. ALVIN S. WHEELER and W. M. OATES (*J. Amer. Chem. Soc.*, 1910, **32**, 770—773).—A study has been made of the action of bromine on anthranilic acid dissolved in glacial acetic acid, both near the m. p. of the acetic acid and also near its b. p. In the former case the product consists of 5-bromo-2-aminobenzoic and 3 : 5-dibromo-2-aminobenzoic acids in the proportion of 2 : 1, whilst in the latter case the proportions are almost exactly reversed.

The *silver* salt and *ethyl* ester, m. p. 187°, of 5-bromo-2-aminobenzoic acid are described. 5-Bromoacetylanthranil has m. p. 134° (compare Bogert and Hand, Abstr., 1906, i, 176). 3 : 5-*Dibromoacetylanthranil*, m. p. 176°, forms long, colourless needles. 3 : 5-*Dibromoacetyl*-2-*aminobenzoic acid*, m. p. 218—219°, obtained by boiling the anil with dilute sodium hydroxide or with glacial acetic acid, crystallises in microscopic needles; its *silver* salt decomposes at about 270°, and its *ethyl* ester has m. p. 74°. E. G.

Esterification. Esterification of Thiolbenzoic Acid by Alcohol and of Benzoic Acid by Mercaptan. E. EMMET REID (*Amer. Chem. J.*, 1910, **43**, 489—504).—In accordance with Henry's hypothesis, the esterification of thiolbenzoic acid by alcohol should take place as follows: $C_6H_5\cdot CO\cdot SH + EtOH \rightleftarrows C_6H_5\cdot C(OH)(SH)\cdot OEt$, and this additive compound may break up into $C_6H_5\cdot CO_2Et + H_2S$ or into $C_6H_5\cdot CS\cdot OEt + H_2O$. In the esterification of benzoic acid by mercaptan, the reaction would be in accordance with the equation: $C_6H_5\cdot CO_2H + EtSH \rightleftarrows C_6H_5\cdot C(OH)_2\cdot SEt \rightleftarrows C_6H_5\cdot CO\cdot SEt + H_2O$.

Qualitative and quantitative experiments have been carried out in order to study these reactions, and to ascertain the mode and extent of esterification of mercaptan.

It has been found that when hydrogen chloride is passed into a solution of thiolbenzoic acid in alcohol, hydrogen sulphide and ethyl benzoate are produced, but ethyl thionbenzoate does not seem to be formed. The reaction proceeds according to the equation:

$$C_6H_5\cdot CO\cdot SH + EtOH = C_6H_5\cdot CO_2Et + H_2S.$$

The same change takes place in the absence of a catalytic agent when thiolbenzoic acid and alcohol are heated in a sealed tube at about 150°. The reaction is not reversible. Thiolbenzoic acid is not produced by the action of hydrogen sulphide on ethyl benzoate, but benzoic acid and mercaptan are obtained thus: $C_6H_5\cdot CO_2Et + H_2S = C_6H_5\cdot CO_2H + EtSH$.

Mercaptan has the power of forming esters, both in presence and absence of a catalytic agent, but is less efficient than alcohol. The reaction between benzoic acid and mercaptan is reversible, and is expressed by the equation: $C_6H_5\cdot CO_2H + EtSH = C_6H_5\cdot CO\cdot SEt + H_2O$. It obeys the law of mass action, and a true equilibrium is reached with about 16·8 per cent. of esterification. E. G.

Synthesis of Aromatic Nitriles. F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1910, **150**, 1241—1243. Compare this vol., i, 257).—Nitriles of the type CHPhR·CN condense with alkyl halides in the presence of sodamide, giving nitriles of the type CPhRR'·CN. The following compounds have been prepared in this way: *a-phenyl-a-ethylbutyronitrile*, $CEt_2Ph\cdot CN$, b. p. 125·5—127°/13 mm., 247—249°/752 mm., $D^{16.5}$ 0·957; *a-phenyl-γ-methyl-a-*iso*propylvaleronitrile*,

$$CH_2Pr^\beta\cdot CPr^\beta Ph\cdot CN,$$

b. p. 148—150°/15 mm., D^{16} 0·932. Similar compounds have also been prepared by the direct action of alkyl halides on phenylacetonitrile in presence of sodamide; thus *n*-propyl bromide furnishes *a-phenyl-a-*n*-propylvaleronitrile*, $CPr^\alpha{}_2Ph\cdot CN$, b. p. 142·5—145°/15 mm., 268—270°/758 mm., D^{14} 0·940; *iso*butyl bromide yields *a-phenyl-γ-methyl-a-*iso*butylvaleronitrile*, $C(CH_2Pr^\beta)_2Ph\cdot CN$, b. p. 152—155°/15 mm., D^{13} 0·931. W. O. W.

Compounds of 3:5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons. OTTO MORGENSTERN (*Monatsh.*, 1910, **31**, 285—294).—3:5-Dinitro-4-hydroxybenzoic acid, the ammonium salt of which exists in a yellow and a red modification, resembles picric acid in forming coloured compounds with aromatic hydrocarbons. The following *compounds* are described: with acenaphthene,

$$C_{12}H_{10},C_7H_4O_7N_2,$$

m. p. 210—211° (decomp.), reddish-orange needles; with naphthalene, $C_{10}H_8,C_7H_4O_7N_2$, m. p. 214—217° (in closed tube), yellow needles; with pyrene, $C_{16}H_{10},C_7H_4O_7N_2$, m. p. 251—252° (decomp.), orange-red needles; with fluorene, $C_{13}H_{10},2C_7H_4O_7N_2$, m. p. 218—221°, pale yellow powder; with retene, $C_{18}H_{18},2C_7H_4O_7N_2$, pale yellow leaflets decomposing at 229—231°; with diphenylene oxide,

$$C_{12}H_8O,2C_7H_4O_7N_2,$$

m. p. 226—232° (decomp.), pale yellow needles; with phenanthrene, $C_{14}H_{10},2C_7H_4O_7N_2$, m. p. 218—222°, reddish-yellow needles; with quinoline, $C_9NH_7,C_7H_4O_7N_2$, citron-yellow powder decomposing at 224·5—225°.

All these compounds are prepared by mixing alcoholic solutions of the constituents and subsequently concentrating the mixture, if necessary; they are more or less unstable, and are partly decomposed by recrystallisation from alcohol, and completely by benzene at the ordinary temperature. C. S.

Lactonoid Anhydrides of Acylated Amino-acids. III. The Lactone of *r*-Benzoylalanine and its Application for the Synthesis of Benzoylated Dipeptides. ERNST MOHR [with FR. STROSCHEIN] (*J. pr. Chem.*, 1910, [ii], 81, 473—500. Compare this vol., i, 116, 117).—The *lactone*, $CHMe<\begin{matrix}N{=}CPh\\ CO{\cdot}O\end{matrix}$, m. p. 39—39·5°, of *r*-benzoylalanine is obtained by heating finely powdered benzoylalanine and acetic anhydride on the water-bath for not more than ten minutes, removing the acetic acid formed and the excess of the anhydride under 0·2—0·5 mm. pressure, and finally distilling the lactone, which passes over at 75—140°/0·2—0·5 mm., and crystallises by keeping in a vacuum desiccator. The lactone develops a temporary intense bluish-violet fluorescence by treatment with *N*/10-sodium hydroxide, and in its chemical behaviour resembles the lactone of benzoyl-α-amino*iso*butyric acid. It easily yields benzoylalanine with hot water, benzoylalanine-amide with ethereal ammonia, ethyl benzoylalanine with alcohol, benzoylalanyl chloride with cold ethereal hydrogen chloride, and Curtius and van der Linden's benzoylalanineanilide with ethereal aniline. Whether prepared in this way or from ethyl benzoylalanine and aniline, or from benzoylalanyl chloride and aniline, the anilide has m. p. 176—176·5°, not 163—165° as given by these authors (Abstr., 1904, i, 883).

Curtius and van der Linden's benzoylalanylglycine (*loc. cit.*) is obtained by adding the lactone to aqueous glycine, keeping the mixture faintly alkaline during the reaction, and subsequently acidifying with 10*N*-hydrochloric acid. In a similar manner, benzoylalanylalanine is obtained from *r*-alanine, and *benzoylalanyl-α-amino*iso*butyric acid*, $NHBz{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CMe_2{\cdot}CO_2H$, m. p. 199—199·5°, from α-amino*iso*butyric acid. By heating with acetic anhydride, the last benzoylated dipeptide alone yields a *lactone*, $NHBz{\cdot}CHMe{\cdot}C<\begin{matrix}N{\cdot}CMe_2\\ O{-}CO\end{matrix}$, m. p. 116—117°, which reacts with ethereal ammonia at 0° to form *benzoylalanyl-α-amino*iso*butyramide*, m. p. 209°.

A comparison is drawn between the properties of benzoyl-α-amino*iso*butyric acid, benzoylalanine, and hippuric acid. The last stands somewhat apart from the first two, being most easily decomposed, but the amide of the first yields a cyclic imide with boiling dilute sodium hydroxide, whilst the amides of the second and the last undergo normal hydrolysis. C. S.

Reaction between Unsaturated Compounds and Organic Zinc Compounds. ELMER P. KOHLER and GERTRUDE L. HERITAGE (*Amer. Chem. J.*, 1910, 43, 475—489).—It has been stated by Kohler and Burnley (this vol., i, 391) that the relation between the character of organic magnesium compounds and their mode of addition to ketones containing the chain C:C·C:O is not easily determined. The results of earlier work show that magnesium compounds containing alkyl groups behave differently from those derived from aromatic compounds which have the halogen directly attached to the nucleus. The former give almost the same amount of the 1 : 4-additive product with any one ketone, whilst magnesium phenyl bromide and magnesium tolyl bromide give relatively a much larger quantity of the 1 : 2-additive product. Attempts have been made to find an explanation for this difference. Owing to certain difficulties which arose, it was decided to substitute zinc for magnesium, and experiments are now described on the action of methyl bromoacetate and zinc on benzylideneacetophenone, benzylidenepropiophenone, and other unsaturated compounds. These ketones give only saturated compounds with the ordinary Grignard reagents, but have been found to yield unsaturated β-hydroxy-esters when they react with zinc and methyl bromoacetate. It has been proved that this difference does not depend on the metal, solvent, or procedure, but is due entirely to the nature of the halogen compounds used.

When a solution of benzylideneacetophenone in benzene is heated with methyl bromoacetate and a slight excess of zinc, 1 : 2-addition takes place with formation of *methyl β-hydroxy-β-phenyl-γ-benzylidenebutyrate*, $CHPh:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, m. p. 126°, which crystallises in slender needles. This ester combines with bromine to form a solid *dibromide*, which on recrystallisation from chloroform is converted into *methyl β-hydroxy-β-phenyl-γ-bromobenzylidenebutyrate*, $CPhBr:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, which forms thick needles, and begins to decompose at about 200°. Magnesium can be used instead of zinc in the reaction between benzylideneacetophenone and methyl bromoacetate, and, in this case, as in the former, only the 1 : 2-additive compound is produced. When magnesium is employed, ether can be used instead of benzene as a solvent, but the manipulation is troublesome and the yield unsatisfactory.

Methyl β-hydroxy-β-phenyl-γ-benzylidenevalerate,

$$CHPh:CMe\cdot CPh(OH)\cdot CH_2\cdot CO_2Me,$$

m. p. 70°, obtained by the action of methyl bromoacetate on benzylidenepropiophenone in presence of zinc and benzene, or magnesium and ether, forms large, lustrous plates.

When ethylideneacetophenone is treated with methyl bromoacetate and zinc, *methyl β-hydroxy-β-phenyl-Δ$^{\gamma}$-hexenoate*,

$$CHMe:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me,$$

m. p. 58°, is produced, which crystallises in long needles; its *bromo-*derivative, $CMeBr:CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me$, m. p. about 175° (decomp.), forms small prisms or plates.

Cinnamaldehyde, when treated in the same way, gives a product which does not solidify, but, on distillation under reduced pressure, loses water and yields methyl cinnamylideneacetate. This aldehyde

reacts similarly with methyl α-bromopropionate to form methyl α-methylcinnamylideneacetate.

Ethyl β-hydroxy-β-methyl-γ-benzylidenebutyrate,
$CHPh:CH \cdot CMe(OH) \cdot CH_2 \cdot CO_2Et$,
b. p. 192°/20 mm., obtained from styryl methyl ketone and ethyl bromoacetate, is a colourless liquid, and on hydrolysis with potassium hydroxide yields phenylmethylbutadiene, m. p. 37°. When this ester is boiled with hydrochloric acid, it is converted into *β-methylcinnamylideneacetic acid*, $CHPh:CH \cdot CMe:CH \cdot CO_2H$, m. p. 153°, which forms small prisms or plates.

The product obtained from benzylidenepinacolin and methyl bromoacetate loses water on distillation under reduced pressure, and yields *methyl β-butylcinnamylideneacetate*, b. p. 210°/20 mm.

Methyl γ-bromo-β-hydroxy-β-phenyl-γ-benzylidenebutyrate,
$CHPh:CBr \cdot CPh(OH) \cdot CH_2 \cdot CO_2Me$,
m. p. 79—80°, prepared from α-bromobenzylideneacetophenone and methyl bromoacetate, forms colourless needles.

Cinnamylideneacetophenone reacts with methyl bromoacetate to form *methyl β-hydroxy-β-phenyl-γ-cinnamylidenebutyrate*,
$CHPh:CH \cdot CH:CH \cdot CPh(OH) \cdot CH_2 \cdot CO_2Me$,
m. p. 112°, which crystallises in slender needles.

Benzylidenedeoxybenzoin and benzylideneacetylmesitylene do not react with methyl bromoacetate in presence of zinc, although they readily give 1 : 4-additive compounds with Grignard reagents.

E. G.

Preparation of Iodoacylsalicylic (*o*-Iodoacyloxybenzoic) Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 221384).—The *o*-bromoacyloxybenzoic acids have been previously described (Abstr., 1909, i, 798); it is now found that *o*-iodoacyloxybenzoic acids can be readily prepared by similar methods, and are of therapeutic value as antirheumatics.

o-*Iodoacetoxybenzoic acid*, $CO_2H \cdot C_6H_4 \cdot O \cdot CO \cdot CH_2I$, obtained by the interaction of iodoacetyl chloride and sodium salicylate in dry benzene solution, forms colourless needles, m. p. 138° (decomp.).

o-α-*Iodo*iso*valeryloxybenzoic acid*, $CO_2H \cdot C_6H_4 \cdot O \cdot CO \cdot CHI \cdot CHMe_2$, colourless crystals, m. p. 102°, is analogously prepared.

F. M. G. M

Piperonylic Acid. E. OERTLY and AMÉ PICTET (*Ber.*, 1910, **43**, 1336—1340).—*Methyl piperonylate*, $CH_2O_2:C_6H_3 \cdot CO_2Me$, forms colourless needles, m. p. 53°. The *mononitro*-derivative, obtained by interaction with fuming nitric acid and acetic acid, crystallises in colourless needles, m. p. 102°, and on reduction by means of tin chloride and acetic acid is converted into *methyl aminopiperonylate*, which separates in silver-grey needles, m. p. 108°. On replacing the amino-group by carboxyl, hydrastic acid is obtained, showing the amino-group to be in position 6.

Methyl cyanopiperonylate is prepared by diazotising the amino-compound in hydrochloric acid solution and adding potassium cyanide, and crystallises in light yellow needles, m. p. 135—136°. Hydrolysis con-

verts this into hydrastic acid, and this affords a convenient process for preparing this acid. Nitration of methyl hydrastate gives the nitro-compound already described.

The position of the bromine atom in bromopiperonal and bromopiperonylic acid (Fittig and Mielch, *Annalen*, 1869, **152**, 49) was unknown previously. The latter compound yields a *methyl* ester separating in colourless crystals, m. p. 87—88°, which substance is also obtainable from methyl aminopiperonylate by diazotisation and decomposition with copper bromide. This fixes position 6 as that of the bromine atom.

Bromonitrocatechol methylene ether, $CH_2O_2{:}C_6H_2(NO_2)Br$, crystallises in yellow needles, m. p. 87°.

Methyl bromonitropiperonylate, $CH_2O_2{:}C_6H(NO_2)Br{\cdot}CO_2Me$, forms yellow needles, m. p. 131°, and on reduction with ammonium sulphide is converted into *methyl bromoaminopiperonylate*, which separates in greyish-white needles, m. p. 92°. E. F. A.

Synthetical Experiments with *o*-Xylylene Cyanide. OSCAR HINSBERG (*Ber.*, 1910, **43**, 1360—1363).—*o*-Xylylene cyanide contains two reactive methylene groups, and therefore condenses in presence of sodium ethoxide with *o*-diketones, keto-acids, and esters of oxalic acids to naphthalene derivatives.

With ethyl oxalate, 1 : 4-*dicyano*-2 : 3-*dihydroxynaphthalene* is formed; this crystallises in a voluminous mass of light yellow plates, m. p. 291°, and shows an intense blue coloration with ferric chloride.

With benzil, 1-*cyano*-2 : 3-*diphenylnaphthalene*-4-*carboxylamide*,

$$C_6H_4<\begin{matrix}C(CN)\!=\!=\!=\!=CPh\\ C(CO{\cdot}NH_2){:}\overset{|}{C}Ph\end{matrix},$$

is formed ; this separates in colourless crystals, m. p. above 290°.

With phenanthraquinone, *cyanonaphthaphenanthrenecarboxylamide* is obtained, crystallising in minute, yellow needles, m. p. 306°. Hydrolysis of these substances to the corresponding carboxylic acids does not take place easily. E. F. A.

Preparation of Alkyl- and Aryl-oxyacylsalicylic [*o*-Aryl-oxyacyloxybenzoic] Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 221385).—The *o*-alkyl- and *o*-aryl-oxyacylbenzoic acids are prepared by the action of the anhydrides, or alkyl- or aryl-oxyparaffin acid chlorides on salicylic acid in the presence or absence of condensing agents.

o-*Phenoxyacetyloxybenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}OPh$, tasteless, colourless needles, m. p. 143°, is prepared by slowly adding phenoxyacetyl chloride to a suspension of sodium salicylate in benzene at 16° with continual stirring during seven hours.

o-*Ethoxyacetyloxybenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}OEt$, colourless needles, m. p. 91°, is analogously prepared from ethoxyacetyl chloride in the presence of dimethylaniline; it has an acid taste, but compares favourably with acetylsalicylic acid in its therapeutic action. F. M. G. M.

Condensation of Ethyl Oxalate with Ethyl Tricarballylate. HENRI GAULT (*Compt. rend.*, 1910, **150**, 1341—1343).—In presence of sodium ethoxide, ethyl oxalate condenses with ethyl tricarballylate to form a mixture of ethyl oxalotricarballylate and ethyl *cyclo*pentandione-1 : 2 : 3-tricarboxylate. Wislicenus (Abstr., 1896, i, 604) gives m. p. 123° for the latter compound, and states that he was unable to effect hydrolysis by acids or alkalis. The present author gives m. p. 127°, and finds that hydrolysis with hydrochloric acid leads to the formation in the first place of *ethyl* cyclo*pentandione*-1 : 2-*dicarboxylate*, $\begin{array}{l}CO\text{———}CO\\ |\\ CH_2\cdot CH(CO_2H)\end{array}\!\!>\!CH\cdot CO_2Et$. This substance has m. p. 137°, and develops a reddish-violet coloration with ferric chloride; it forms a *disemicarbazone* and a *diphenylhydrazone*, m. p. 190° (decomp.). Prolonged hydrolysis of the triethyl ester results in the formation of cyclo*pentandionecarboxylic acid*, $\begin{array}{l}HO\cdot C{=}CH\\ \;\;\;\;\;\;|\\ \;\;\;\;CO{-}CH\end{array}\!\!>\!CH\cdot CO_2H$. This has m. p. 137°, gives a red coloration with ferric chloride, and forms a hygroscopic *disemicarbazone* and a *diphenylhydrazone* having m. p. 220° (decomp.). W. O. W.

Action of Alcoholic Ammonia on Acetyltannin and Triacetylgallic Acid. MAXIMILIAN NIERENSTEIN (*Ber.*, 1910, **43**, 1688—1690).—By the action of alcoholic ammonia on acetyltannin at the ordinary temperature, a mixture of products is formed; at the temperature of the water-bath, gallic acid and gallamide are obtained with other products.

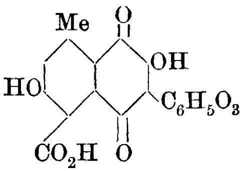
Triacetylgallic acid, when treated with 3 mols. of alcoholic ammonia in the cold, forms *diacetylgallic acid*, crystallising in tiny needles, m. p. 174—176°; this gives a dark green coloration with ferric chloride, and a red coloration with potassium cyanide. It is suggested that the *p*-acetyl group is the one eliminated. E. F. A.

Schiff's Digallic Acid or Artificial Tannin. PIETRO BIGINELLI (*Ber.*, 1910, **43**, 1541—1543).—A reply to Nierenstein (this vol., i, 265). The author maintains that Schiff's digallic acid contains an arsenic compound (compare Biginelli, Abstr., 1909, i, 801). The reason why Nierenstein could not detect arsenic was that he did not destroy the organic matter. J. J. S.

Dye of Kermes. OTTO DIMROTH (*Ber.*, 1910, **43**, 1387—1401).—*Kermesic acid*, $C_{18}H_{12}O_9$, the name given by the author to the dye isolated by a slightly modified form of Heise's process from kermes (*Coccus ilicis*), is very similar to carminic acid in tinctorial properties and in its absorption spectrum, but differs from it by its solubility in ether, a property which suggests that the molecule of kermesic acid is smaller than that of carminic acid, and contains fewer hydroxyl groups. Kermesic acid crystallises in brick-red needles, darkens at 250° without melting, and dissolves without decomposition in concentrated sulphuric acid, forming a violet-red solution, the absorption spectrum of which is very similar to that of carminic acid, and both spectra experience the same change by the addition of boric acid.

Kermesic acid is a monocarboxylic acid, which forms a tetra-acetyl *derivative*, $C_{18}H_8O_9Ac_4$, m. p. 245°, and does not contain methoxyl groups. The *disodium* and the *barium* salts are described. The red colour of a dilute alcoholic solution of the acid remains unchanged by the addition of one equivalent of potassium hydroxide, and becomes violet when two equivalents have been introduced. The acid is reduced by hydriodic acid to a red *substance*, $C_{18}H_{12}O_8$, which decomposes at 275°, and is oxidised by warm concentrated nitric acid to nitrococussic acid, the longest known degradation product of carminic acid.

The paper deals mainly with the degradation products of kermesic acid identical with those of carminic acid; an examination of these products leads the author to suggest the annexed formula for kermesic acid, similar to that of carminic acid. Several methylated derivatives can be obtained from kermesic acid. *Kermesic acid trimethyl ether*, $C_{21}H_{18}O_9$, m. p. 310°, is obtained by boiling a suspension of potassium kermesate in toluene with methyl sulphate, digesting the crystalline product with potassium carbonate, and decomposing the insoluble portion with warm dilute hydrochloric acid; the ether is finally crystallised from glacial acetic acid, from which it separates in orange-red needles. Its oxidation by hot potassium permanganate leads to the formation of two acids. One is *methyl cochenillate methyl ether*,



$$OMe\cdot C_6HMe(CO_2H)_2\cdot CO_2Me,$$

which yields an *anhydride*, m. p. 149°, at its m. p., 178—180°, and is hydrolysed by 25% potassium hydroxide to *cochenillic acid methyl ether*, $C_{11}H_{10}O_7$, m. p. 200° (decomp.); both ester and acid are converted into hydroxyuvitic acid by hydriodic acid, D 2·0. The other acid is a *methyl* ester of cresotinglyoxyldicarboxylic acid methyl ether,

$$OMe\cdot C_6HMe(CO_2H)(CO_2Me)\cdot CO\cdot CO_2H,$$

m. p. 108—110° (the hydrated acid has m. p. 86°), which forms a *phenylhydrazone*, m. p. 183°, and is oxidised by sodium carbonate and potassium permanganate to methyl cochenillate methyl ether.

[With HAMBURGER.]—The last-mentioned compound is obtained, together with cochenillic acid methyl ether, when methyl carminate methyl ether is heated on the water-bath with nitric acid. C. S.

Influence of Ortho-substituents on the Formation of Aldehyde Diacetates. ERNST SPÄTH (*Monatsh.*, 1910, **31**, 191—194. Compare Wegscheider and Späth, this vol., i, 155).—Fischer and Giebe (Abstr., 1898, i, 311) have shown that ortho-substituents in an aldehyde facilitate the formation of acetals, with the single exception of *s*-trimethylbenzaldehyde. The author finds that the negative nitro-groups in 2 : 4 : 6-trinitrobenzaldehyde (Sachs and Everding, Abstr., 1902, i, 377) retard the formation of a diacetate from the aldehyde, acetic anhydride, and two drops of sulphuric acid. A better yield of the *diacetate*, $C_6H_2(NO_2)_3\cdot CH(OAc)_2$, is obtained when the mixture is kept for fifteen hours; it crystallises in needles, m. p. 117—118°.

J. J. S.

Chemical Action of Light. XVIII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1910, **43**, 1536—1541 ; *Atti R. Accad Lincei*, 1910, [v], **19**, i, 645—650. Compare Abstr., 1901, i, 36 ; 1903, i, 562).—Solutions of benzophenone in aromatic hydrocarbons undergo change when exposed to light in tubes for some months. In all cases benzopinacone is formed, and the hydrocarbon undergoes condensation. With a solution in cymene, a dicymyl, probably identical with Cannizzaro and Rossi's (*Annalen*, 1862, **121**, 251), is formed. With a toluene solution the products are benzopinacone, Cannizzaro and Rossi's dibenzyl, m. p. 52°, and diphenylbenzylcarbinol (Hell and Wiegandt, Abstr., 1904, i, 490), which is formed by the addition of a molecule of toluene to one of benzophenone.

Benzophenone and ethylbenzene yield benzopinacone, the hydrocarbon, $C_{16}H_{18}$, m. p. 124° (Paterno and Chieffi, this vol., i, 42), and the additive product, $C_{21}H_{20}O$, which forms large, monoclinic crystals

$$[a:b:c = 1{\cdot}8207:1:0{\cdot}6671\ ;\ \beta = 86°11'].$$

When heated at 300° this compound is partly converted into benzophenone and ethylbenzene, but is also partly decomposed into water and a *hydrocarbon*, $C_{21}H_{18}$, m. p. 88°.

Benzophenone and *p*-xylene give benzopinacone, *pp'*-dimethyldibenzyl, and the additive compound, $OH{\cdot}CPh_2{\cdot}CH_2{\cdot}C_6H_4Me$, *diphenyl*-p-*methylbenzylcarbinol*, m. p. 113°, b. p. 258—260°/24 mm.

A mixture of toluene and acetone yields dibenzyl. J. J. S.

Ketonic Derivatives of Benzoic and Phenylacetic Acids. JEAN B. SENDERENS (*Compt. rend.*, 1910, **150**, 1336—1338. Compare Abstr., 1909, i, 286, 627 ; this vol., i, 11, 179, 318).—The catalytic method already described is advantageous for the preparation of the undermentioned ketones in a state of purity. The corresponding oximes and semicarbazones are best prepared by heating a solution of the ketone in 85% alcohol with pure sodium aluminate and the hydrochloride of hydroxylamine or semicarbazide. Acetophenone ; propiophenone, hitherto described as a liquid, crystallises in lamellæ, m. p. 14·5°, b. p. 215°/746 mm. (corr.), D_4^{16} 1·008 ; phenyl *n*-propyl ketone, m. p. 8·5°, b. p. 229°/746 mm. (corr.), D_4^0 1·001 ; phenyl *iso*propyl ketone, b. p. 220°/746 mm., D_4^0 0·999 ; phenyl *iso*butyl ketone, b. p. 236·5°/746 mm. (corr.), D_4^0 0·985, the oxime has m. p. 64·5.

Dibenzyl ketone is obtained in theoretical yield by passing the vapour of phenylacetic acid over thorium oxide at 430° ; the *phenylhydrazone* has m. p. 121° ; the *semicarbazone*, m. p. 123°. Phenyl benzyl ketone, D_4^0 1·019, gave a *semicarbazone*, decomposing at 165—180° ; α-phenylbutan-β-one, b. p. 230°/755 mm. (corr.), D_4^0 1·002, gave a *semicarbazone*, m. p. 135·5° (decomp.) ; *α-phenylpentan-β-one*, b. p. 244°/760 mm., D_4^0 0·984, the *semicarbazone* has m. p. 82° ; *α-phenyl-γ-methylbutan-β-one*, b. p. 237°/760 mm. (corr.), D_4^0 0·985, the *semicarbazone* has m. p. 126° ; *α-phenyl-δ-methylpentan-β-one*,

$$CH_2Ph{\cdot}CO{\cdot}CH_2Pr^{\beta},$$

b. p. 250·5°/760 mm. (corr.), D_4^0 0·969, gave a *semicarbazone*, m. p. 80°, and a *phenylhydrazone*, crystallising in yellow needles, m. p. 67°.

W. O. W.

Duplobenzylidenethioacetone; a Correction. EMIL FROMM (*Ber.*, 1910, **43**, 1759. Compare Abstr., 1907, i, 710).—The so-called duplobenzylidenethioacetone is a mixture of a non-basic substance and one or more basic compounds which form salts with mineral acids. It is now found that these compounds contain about 4% of nitrogen, which explains their basic properties, and renders the explanation given formerly (*loc. cit.*) quite unnecessary. E. F. A.

Preparation and Properties of 2:2-Dialkyl-1-hydrindones or 2:2-Dialkyl-1-indanones. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1910, **150**, 1472—1478. Compare Kipping, Trans., 1894, **65**, 480, Proc., 1901, **17**, 181; Haller and Bauer, Abstr., 1909, i, 109, 655).—Alkylation of 1-hydrindone by means of an alkyl halide in presence of sodamide leads to the production of a dialkyl derivative identical with that obtained by Kipping's method from a substituted β-phenylpropionic acid; thus 2 : 2-*dimethyl*-1-*hydrindone*,

$$C_6H_4<\substack{CH_2\\CO}>CMe_2,$$

was prepared in 80% yield by warming an ethereal solution of hydrindone with sodamide in absence of air, boiling with methyl iodide for an hour, isolating the product, b. p. 116—120°/16 mm., and repeating the methylation, using benzene as the solvent. The compound was also obtained by the action of aluminium chloride on β-*phenyl*-$\alpha\alpha$-*dimethylpropionyl chloride*, m. p. 5°, b. p. 125—126°/15 mm. 2:2-Dimethylhydrindone forms magnificent crystals, m. p. 44—45°; when heated with sodamide in benzene it yields β-phenyl-$\alpha\alpha$-dimethylpropionamide. The *semicarbazone* forms needles, m. p. 209—210°.

2:2-*Diethylhydrindone*, $C_{13}H_{16}O$, has m. p. 7°, b. p. 138°/13 mm., and does not form a semicarbazone. The following compounds are described in connexion with its preparation.

β-*Phenyl*-α-*ethylpropiophenone*, $COPh\cdot CHEt\cdot CH_2Ph$, arising from the action of benzyl chloride on phenyl n-propyl ketone in presence of sodamide, has b. p. 183—185°/14 mm., and forms an *oxime*, m. p. 70°. β-*Phenyl*-α-*benzyl*-α-*propylpropiophenone*, $COPh\cdot CPr^{\alpha}(CH_2Ph)_2$, is also formed in this reaction, and crystallises in needles, m. p. 67—68°. β-*Phenyl*-$\alpha\alpha$-*diethylpropiophenone*, $COPh\cdot CEt_2\cdot CH_2Ph$, obtained as a liquid, b. p. 190—202°/13 mm., by ethylation of β-phenyl-α-ethylpropiophenone, slowly crystallises in tablets, m. p. 80—80·5°. β-*Phenyl*-$\alpha\alpha$-*diethylpropionyl chloride* has b. p. 148°/13 mm. W. O. W.

Synthesis of the Higher Indandiones. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1910, **373**, 291—336).—Benzene and other aromatic hydrocarbons readily condense with diethylmalonyl chloride in the presence of aluminium chloride, yielding indandiones as the chief products in accordance with the equation:

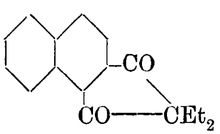
$$C_6H_6 + CEt_2(COCl)_2 = C_6H_4<\substack{CO\\CO}>CEt_2 + 2HCl,$$

carbon disulphide usually being employed as the solvent; thus equal molecular quantities of benzene and the chloride yield a very small amount of $\gamma\gamma$-*dibenzoylpentane*, $CEt_2(COPh)_2$, m. p. 103—104°, the chief product being 2:2-*diethylindan*-1; 3-*dione*, $C_6H_4<\substack{CO\\CO}>CEt_2$,

b. p. 147—156°/10 mm., D^{15} 1·062, which forms a *dioxime*, m. p. 142—144°, yields phthalic acid by oxidation with nitric acid at 130—140°, and benzoic acid by heating with concentrated potassium hydroxide. When two molecular proportions of benzene are employed in the condensation, a third product is obtained, *β-hydroxy-ββ-diphenyl-αα-diethylpropiolactone*, $CEt_2<\!\substack{CPh_2\\CO-}\!\!>O$, m. p. 89—90°.

Condensation with *p*-cymene yields only *4-methyl-2 : 2-diethyl-7-*iso*propylindandione*, $C_6H_2MePr^{\beta}<\!\substack{CO\\CO}\!>CEt_2$, m. p. 37—38·5°, the constitution of which follows from its oxidation to prehnitic acid by nitric acid at 130°.

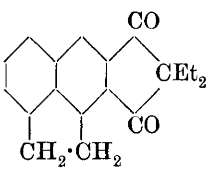
With more complex hydrocarbons increasing difficulty is encountered in ascribing constitutions to the resulting indandiones. Naphthalene yields three isomeric products: I, a yellow *solid*, m. p. 79—81°, which receives the annexed constitution on account of its oxidation to prehnitic acid; II, a colourless *solid*, m. p. 120·5—122°, in which condensation has occurred at positions 2 and 3 of the naphthalene nucleus, since boiling concentrated aqueous potassium hydroxide decomposes the substance, forming *β-naphthoyldiethylacetic acid*,



$$C_{10}H_7\cdot CO\cdot CEt_2\cdot CO_2H,$$

m. p. 128—130°, which is oxidised by nitric acid at 120—140° to trimellitic acid; III, an *oil*, b. p. 210—212°/6 mm., which is very stable to alkali, and receives the only remaining possible constitution in which condensation has occurred in the *peri*-position.

The constitutions of the two indandiones obtained from acenaphthene follow very much from analogy to those of the naphthindandiones; *α-diethylacenaphthindandione*, m. p. 153—155°, is yellow, and is converted by concentrated potassium hydroxide into *α-diethylacenaphthindandionic acid*, $C_{19}H_{20}O_3$, m. p. 163—164°; it receives the annexed constitution. *β-Diethylacenaphthindandione*, m. p. 109—111°, is intensely yellow, and has the group $CEt_2<\!\substack{CO\\CO}$ in positions 1 : 2.



The condensation of anthracene (without carbon disulphide) yields only *diethylanthraceneindandione*, $C_{21}H_{18}O_2$, m. p. 104—105°, which is oxidised by chromic and acetic acids to the *quinone*, $C_{21}H_{16}O_4$, m. p. 193—194°, and is converted by concentrated potassium hydroxide into *diethylanthraceneindandionic acid*, $C_{21}H_{20}O_3$, m. p. 209—210° (decomp.). The condensation of phenanthrene yields *diethylphenanthreneindandione*, $C_{21}H_{18}O_2$, m. p. 137—139°, b. p. 254—273°/10 mm., which is converted by potassium hydroxide into *diethylphenanthreneindandionic acid*, m. p. 155°, and by chromic and acetic acids into the *quinone*, $C_{21}H_{16}O_4$, m. p. 223—224°, which is further oxidised by the acids, when hot, to the *diethylindandione* of diphenic acid,

$$C_{12}H_6(CO_2H)_2<\!\substack{CO\\CO}\!>CEt_2,$$

m. p. 235°. The condensation with retene yields *diethylreteneindandione*, $C_{25}H_{26}O_2$, m. p. 134—135°, which yields the *quinone*, $C_{25}H_{24}O_4$, m. p. 193—194°, by oxidation.

The condensation with thiophen yields two products, neither of which is an indandione : one is *γγ-dithiophenoylpentane*,

$$CEt_2(CO\cdot C_4SH_3)_2,$$

m. p. 152—153°; the other, *γ-thiophenoylpentane*,

$$CHEt_2\cdot CO\cdot C_4SH_3,$$

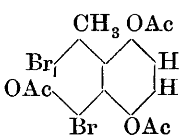
b. p. 146—147°/22 mm., D^{18} 1·058, and n_D 1·53153.

Many of these indandiones and indandionic acids develop characteristic colorations with concentrated sulphuric acid; tabulated lists of these are given. C. S.

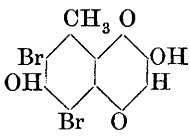
Constitution of β-Bromocarmin. Georg Rohde and G. Dorfmüller (*Ber.*, 1910, **43**, 1363—1370).—β-Bromocarmin was considered by von Miller and Rohde (Abstr., 1894, i, 94) to be a substituted bromohydroxy-α-naphthaquinone derivative; Liebermann and Voswinckel (Abstr., 1897, i, 539; 1909, i, 487) regarded it as an indone derivative.

β-Bromocarmin, when warmed with acetic anhydride and a drop of sulphuric acid, forms an *acetyl* derivative crystallising in yellow needles, m. p. 229°; this is no longer acid, and the composition is such that it cannot be derived from a substance of the formula proposed by Liebermann and Voswinckel.

By reduction of β-bromocarmin with zinc dust and acetic acid and subsequent acetylation, a *compound*, $C_{17}H_{14}O_6Br_2$, crystallising in minute, colourless needles, m. p. 208°, is obtained, which has the annexed formula, agreeing with the constitution of Miller and Rhode, but which is not in agreement with the indone structure.



Hydrolysis and oxidation by means of alkaline hydrogen peroxide yields a *substance*, crystallising in orange prisms, m. p. 258°, in which probably a hydroxyl group has entered the quinone nucleus (annexed formula).



On acetylation, greenish-yellow needles, m. p. 233°, of a *diacetyl* derivative were obtained. The hydrolysis and oxidation product is only slightly attacked by bromine, small quantities of α-bromocarmin being formed.

Both this product and β-bromocarmin yield naphthalene when distilled with zinc dust.

On reduction and subsequent acetylation of bromohydroxy-α-naphthaquinone a substance crystallising in colourless needles, m. p. 159°, is obtained, in which neither hydroxyl nor bromine is replaced by hydrogen. This behaviour is attributed to the negative groups in the second nucleus of bromohydroxynaphthaquinone. E. F. A.

Action of Magnesium Derivatives of *o*- and *p*-Bromoanisole on Anthraquinone and β-Methylanthraquinone. Albin Haller and A. Comtesse (*Compt. rend.*, 1910, **150**, 1290—1295. Compare Abstr., 1904, i, 314, 659, 660; Guyot and Staehling, Abstr., 1905, i, 885; 1906, i, 17).—The organo-magnesium derivatives of *o*- and

p-bromoanisole react with anthraquinone and methylanthraquinone in the same manner as the magnesium derivatives of benzene and naphthalene already studied.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyldihydroanthracene*,

$$C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)(OH)\\C(C_6H_4\cdot OMe)(OH)\end{matrix}>C_6H_4,$$

obtained from anthraquinone and magnesium *p*-anisole bromide, is a colourless, microcrystalline substance, m. p. 267°. Sulphuric acid develops a red coloration, changing to violet, then to blue, and becoming green on dilution. Dimethylaniline gives a blue coloration, changing to rose-violet. The *diethyl ether* has m. p. 280—281°.

9 : 10-*Dihydroxy*-9 : 10-*di*-o-*anisyldihydroanthraquinone*, occurring in microscopic crystals, m. p. 285°, forms a blue solution in sulphuric acid, changing to green, and becoming brown on heating or dilution. When boiled with zinc and glacial acetic acid it yields *di*-o-*anisylanthracene*, $C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)\\|\\C(C_6H_4\cdot OMe)\end{matrix}>C_6H_4$, crystallising in yellow needles, m. p. 280—281°. *Di*-p-*anisylanthracene* forms yellow needles, m. p. 279—280°, and, like the ortho-compound, dissolves sparingly in organic solvents, giving bluish-violet solutions, which show magnificent fluorescence.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyl*-2-*methyldihydroanthracene*,

$$C_6H_4<\begin{matrix}C(C_6H_4\cdot OMe)(OH)\\C(C_6H_4\cdot OMe)(OH)\end{matrix}>C_6H_3Me,$$

prepared from β-methylanthraquinone, separates from benzene in efflorescent crystals, m. p. 208°; with sulphuric acid it develops an intense, eosin-red coloration, changing to blue, and on dilution to green. Dimethylaniline gives a green coloration, changing to brown. The isomeric *di*-o-*anisyl* compound forms efflorescent crystals, m. p. 260°, and gives an intense malachite-green coloration with sulphuric acid; glacial acetic acid and dimethylaniline give a brilliant-green coloration, changing to olive. *Di*-p-*anisyl*-β-*methylanthracene* crystallises in yellow needles, m. p. 214—215°; its solutions are reddish-violet and highly fluorescent. *Di*-o-*anisyl*-β-*methylanthracene* resembles the para-isomeride, and has m. p. 165—167°.

Attempts to convert the foregoing diols into diphenols by heating with hydrogen bromide were unsuccessful. W. O. W.

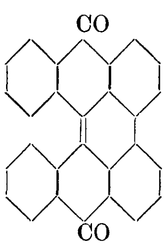
Attempts to Prepare Thiazine Dyes of the Anthraquinone Series. EDUARD LAUBÉ and J. LIBKIND (*Ber.*, 1910, 43, 1730—1734).—Whereas diamino-1-anilinoanthraquinone reacts readily with sulphur, forming a thiazine dye, the 2-anilino-derivative gives a variety of products, and only very little sulphur compound. Apparently, an amino-group is eliminated, and the basic properties are much lessened, so that it is doubtful whether the sulphur compounds are true thiazine dyes.

1-*op*-Dinitroanilinoanthraquinone, prepared from aminoanthraquinone and chlorodinitrobenzene in presence of copper acetate or copper powder, separates in well formed, brown, lustrous needles, m. p. 341° (corr.). The corresponding 2-op-*dinitroanilinoanthraquinone* crystallises in beautiful yellow, lustrous needles, m. p. 275° (corr.).

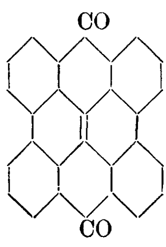
1-op-*Diaminoanilinoanthraquinone*, obtained by reducing the nitro-compound with sodium sulphide, forms small, reddish-violet crystals, m. p. above 350°, which give a reddish-violet, metallic streak on glazed porcelain. 2-op-*Diaminoanilinoanthraquinone* forms black needles, m. p. 255°, and makes a brownish-red streak on porcelain.

The 1-*anthrathiazine*, $C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2{<}{\substack{NH\\S}}{>}C_6H_3\cdot NH_2$, is obtained from 1-*op*-diaminoanilinoanthraquinone by heating it at 150—200° with sulphur and sodium sulphide. It dyes cotton in fast green shades. The corresponding dye from the 2-anilino-compound is obtained in small quantities only, and dyes cotton in fast brown shades. E. F. A.

Vat Dyes of the Anthracene Series. XV. *meso*Benzdianthrone (Helianthrone), *meso*Naphthadianthrone, and a New Method of Preparing Flavanthren. ROLAND SCHOLL, JOHANNES MANSFELD [and, in part, JULIUS POTSCHIWAUSCHEG] (*Ber.*, 1910, 43, 1734—1746. Compare this vol., i, 264, 272).—Copper powder in presence of concentrated sulphuric acid at the ordinary temperature acts as a reducing agent on dianthraquinonyl, eliminating two oxygen atoms and forming a binuclear quinone, which it is proposed to name 1 : 9-, 1′ : 9′-, or *meso*benzdianthrone (annexed formula). The compound was at first described under the name helianthrone. It contains the two chromophores in conjugated position, and, accordingly, should give only one reduction product of the anthrahydroquinone type, namely, a dihydro-compound. Only one, a green, reduction vat is formed by *meso*benzanthrone.



When heated with anhydrous aluminium chloride for a short time at 140—145°, it is quantitatively converted into 1 : 9 : 8-, 1′ : 9′ : 8′-, or *meso*naphthadianthrone (annexed formula). On nitrating 1 : 1′-dianthraquinonyl, a mixture of dinitro-derivatives is obtained, which, when reduced with potassium sulphide, shows the presence of small quantities of flavanthren. The unknown 2 : 2′-*dinitro*-1 : 1′-*dianthraquinonyl* must have been formed and reduced to the corresponding 2 : 2′-*diamino*-derivative, which undergoes spontaneous change into flavanthren.



1 : 1′-Dianthraquinonyl was prepared by reduction of iodoanthraquinone in yellow or brownish-yellow crystals, m. p. 340—345°. The *tetrabromide*, produced by bromination in acetic acid in presence of iodine, forms dark needles. On nitration, in addition to the 2 : 2′-dinitro-derivative which was not isolated, two other isomerides in about equal quantities were obtained. *α-Dinitro-1 : 1′-dianthraquinonyl* is a yellow powder, m. p. above 360°, and insoluble in boiling acetic acid. On reduction, the corresponding *diamino*-compound, a glistening, red powder, is formed. *β-Dinitro-1 : 1′-dianthraquinonyl* is a yellow powder, decomp. 240°, soluble in boiling acetic acid. The *diamino*-compound is a dark brownish-red powder.

1 : 1′-Dianthraquinonyl may be reduced to meso*benzdianthrone* by

means of zinc dust and acetic acid at 60—70°, stannous chloride at 150°, zinc dust and fused zinc chloride at 280—290°, alcoholic potassium hydroxide at 200°, or, best of all, copper powder and concentrated sulphuric acid. *meso*Benzdianthrone dissolves in organic solvents to yellow solutions with a green fluorescence. *Tetrabromo*-meso*dianthrone* forms yellowish-brown needles, and yields a green reduction vat which dyes glistening, golden-yellow shades.

The green vat produced by reducing *meso*benzdianthrone with hot alkaline sodium hyposulphite is a dihydro-derivative, since it forms *di*-p-*bromobenzoyldihydro*meso*benzdianthrone* on treatment with bromobenzoyl chloride.

meso*Naphthadianthrone* forms brown needles from nitrobenzene; it dissolves in concentrated sulphuric acid with a red coloration and brown fluorescence. E. F. A.

Reduction Products of *meso*Benzdianthrone (Helianthrone). JULIUS POTSCHIWAUSCHEG (*Ber.*, 1910, **43**, 1746—1748).—*meso*Benzdianthrone when shaken with acetic anhydride and zinc dust at the ordinary temperature yields *diacetyldihydro*meso*benzdianthrone* in the form of a brown powder soluble in chloroform or acetic anhydride with an olive-green or green fluorescence, and in concentrated sulphuric acid with a green coloration which becomes violet above 200°.

Reduction of *meso*benzdianthrone in boiling acetic anhydride yields *tetrahydro*meso*benzdianthrone* in the form of a black, amorphous *acetyl* derivative, which is hydrolysed by methyl-alcoholic potassium hydroxide. The blackish-brown, amorphous powder shows a brownish-green fluorescence in chloroform; the solution in concentrated sulphuric acid is green, and becomes brown on heating at 240—260°.

When the reduction is prolonged for thirty hours, the *acetyl* derivative of *hexahydro*meso*benzdianthrone* is obtained as a brown, amorphous powder, and hydrolysed by prolonged boiling with methyl-alcoholic potassium hydroxide. E. F. A.

Dihydrocuminyl Alcohol, Nerol, and Terpineol in Bergamot Oil. FRITZ ELZE (*Chem. Zeit.*, 1910, **34**, 538).—In preparing "terpeneless bergamot oil," an ester fraction, D^{15} 0·896, $\alpha = -10°45'$, was obtained, which on hydrolysis yielded a mixture of alcohols, D^{15} 0·890, $\alpha = -10°$. From this, dihydrocuminyl alcohol and nerol were isolated by conversion into phthalic acid esters, hydrolysis of these, and fractionation of the resulting mixture under reduced pressure. The portion of the original alcoholic mixture which did not react with phthalic anhydride was identified as terpineol by conversion into the phenylurethane. T. A. H.

Constituents of Ethereal Oils. Eksantalic Acid, $C_{12}H_{18}O_2$, Eksantalal, $C_{12}H_{18}O$, and Derivatives. FRIEDRICH W. SEMMLER (*Ber.*, 1910, **43**, 1722—1725. Compare Abstr., 1909, i, 239).—To establish the constitution of eksantalic acid the crude product obtained by the oxidation of santalol with permanganate was reduced with sodium and alcohol to *dihydroeksantalic acid*, $C_{12}H_{20}O_2$, b. p. 164—166°/10 mm. The methyl ester was further reduced to *dihydroeksantalol*, $C_{12}H_{22}O$, b. p. 140—142°, D^{20} 0·9689, n_D 1·48905.

The crude ozonide of santalol was decomposed by steam, and two products obtained, one being *eksantaloide*, m. p. 157°, and the other, separated by means of the bisulphite compound, *eksantalal*, $C_{12}H_{18}O$, b. p. 109—110°/10 mm., D^{20} 0·9845, n_D 1·48519, $\alpha_D = +13·5°$ (in 100 mm. tube). Heating with acetic anhydride and sodium acetate forms enol-*eksantalal acetate*, $C_{12}H_{17}O·CO·CH_3$, b. p. 130—132°/10 mm., D^{20} 1·018, which on oxidation with permanganate gives *noreksantalic acid*,

$C_{11}H_{16}O_2$,

b. p. 143—145°/10 mm., m. p. 93°, α_D −12·3° (100 mm. tube, 50% solution). The *methyl* ester has b. p. 102—104°/10 mm., D^{20} 1·023, n_D 1·47348, α_D −25·5° (100 mm. tube). E. F. A.

Chemical Action of Light. XVII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1910, **43**, 1340—1350; *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 532—539).—Camphor in dilute aqueous alcoholic solution in sealed tubes was exposed to the action of light for some months. The products of the reaction were acetaldehyde and campholenaldehyde, $C_{10}H_{16}O$, which forms a hydroxamic acid, $C_{10}H_{17}O_2N$, crystallising in large, colourless, fatty, lustrous plates, m. p. 118°, and is hydrolysed by dilute sulphuric acid to campholenic acid and dihydrocampholenolactone. The third product of the action of light is a *ketone*, $C_{10}H_{16}O$, which is an oil, b. p. 203—204°, and forms a *semicarbazone*, crystallising in colourless, minute needles, m. p. 151—152°. On oxidation, the ketone forms a *dibasic acid*, $C_{10}H_{16}O_5$, crystallising in colourless prisms, m. p. 133—134°.

Fenchone under similar conditions gave rise to carbon monoxide in considerable quantity, and to small quantities of *fenchone hydrate*, $C_{10}H_{18}O_2$, crystallising in plates, m. p. 138—139°. This glycol forms a *dibenzoate*, m. p. 99°, and a *dicarbanilate*, m. p. 206° (decomp.).

Exposure to light has practically no effect on methyl *iso*butyl ketone, mesityl oxide, or methylheptenone, but pinacolin undergoes decomposition into butylene and acetaldehyde. E. F. A.

Caryophyllene. II. CARL W. HAARMANN (*Ber.*, 1910, **43**, 1505—1510. Compare Abstr., 1909, i, 400).—Caryophyllene glycol, m. p. 120°, which had been kept in a closed bottle for four years, was found to be largely transformed into a syrup, probably $C_{14}H_{22}O_3$, and a mixture of two monobasic acids, $C_{14}H_{22}O_5$. The one acid is identical with that already described (*loc. cit.*) as melting at 201—202°; the other is much more readily soluble in ether, crystallises from acetone, and has m. p. 152°. Both acids, when heated with 5% sulphuric acid, lose water and yield anhydro-acids, $C_{14}H_{20}O_4$, melting respectively at 102—103° and 106°, whereas a mixture of the two has m. p. 74—78°.

A dibasic *acid*, $C_{14}H_{20}O_5$, is formed when the acid 201—202° is oxidised with nitric acid (D = 1·48); it forms glistening, hard crystals, m. p. 225°. When the acid, m. p. 152°, is oxidised in a similar manner, a dibasic *acid*, $C_{14}H_{20}O_5$, is obtained as slender needles, m. p. 182°. This acid is quite stable towards permanganate and mixtures of nitric and sulphuric acids.

The acids m. p. 201—202° and 152° can be obtained in the

proportions 1 : 8 by shaking an ethereal solution of carophyllene glycol with a few drops of concentrated sulphuric acid and oxidising the resulting oil with 5% permanganate solution.

When the glycol is oxidised with permanganate, the only acid product formed is the one with m. p. 171°. The statement that two acids, m. p. 201—202° and 162°, are formed is incorrect, as their formation in previous experiments was due to the fact that the glycol had been kept for some time and had undergone change.

J. J. S.

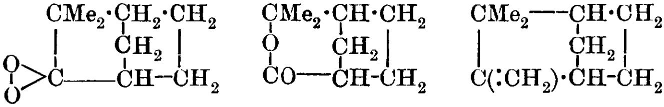
Rotatory Power of Pinene Hydrochloride. Gustave Vavon (*Compt. rend.*, 1910, **150**, 1428—1430. Compare this vol., i, 400; Ahlström and Aschan, Abstr., 1906, i, 442).—A comparison has been made in the case of a number of fractions obtained by crystallisation of the hydrochlorides from French, German, and American turpentines between the rotatory power of the hydrochloride and that of the corresponding pinene and of the product of hydrogenation. The results are given in tabular form, and show that α- and β-pinene yield equal amounts of the same hydrochloride. Similar results have been obtained from a study of the hydrobromides.

W. O. W.

Oxidation of Camphene with Ozone. Carl D. Harries and John Palmén (*Ber.*, 1910, **43**, 1432—1434. Compare Semmler, Abstr., 1909, i, 170).—When an acetic acid solution of pure camphene is treated with ozone at 10°, and the solution of the ozonide then heated on the water-bath, both dimethylnorcampholide—50% (Komppa and Hintikka, Abstr., 1909, i, 301)—and camphenilone are obtained.

The dimethylnorcampholide (δ-hydroxycamphenilonolactone) and not the free hydroxy-acid is regarded as the direct product of decomposition, and its formation is attributed to the peroxide decomposition of the ozonide into peroxide (I), which is transformed readily into the isomeric lactone (II) (compare Harries and Franck, Abstr., 1909, i, 132).

The formation of this lactone is in harmony with Tiemann's camphene formula (III), and the conversion of bornyl chloride into camphene involves a pinacoline transformation.



(I.) (II.) (III.)

Camphenilone was isolated as its *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 222—223°.

J. J. S.

Loango Copal. M. Willner (*Arch. Pharm.*, 1910, **248**, 265—276).—Loango copal, acid number 106·4—114·8 (direct), 114·8—120·4 (indirect), and saponification number 126·0—134·4 (hot), 142·8—154·0 (cold, after twenty-four hours), dissolves completely in

pyridine or quinoline. In its examination it is extracted first by ether, which dissolves 74·9%, and then with ether-alcohol, which dissolves the remainder with the exception of about 2%, consisting of inorganic matter containing sodium, potassium, calcium, magnesium, iron, and silica.

The ethereal abstract is treated successively with 0·5% ammonium carbonate, sodium carbonate, and sodium hydroxide. From the ammonium carbonate solution about 30% of crude acids have been obtained, from which the following have been isolated. *α-Loangocopalic acid*, $C_{20}H_{36}O_2$, m. p. 134°, a monobasic acid containing one ethylenic linking, forms a lead salt insoluble in alcohol, and has acid number 154·0—158·2 (direct), 164·9—165·8 (indirect), saponification number 177·2—177·8 (cold), 180·0—181·4 (hot), and iodine number 78·4—80·4. *β-Loangocopalic acid*, $C_{15}H_{30}O_2$, m. p. about 56°, a monobasic acid containing one ethylenic linking, forms a lead salt soluble in alcohol, and has acid number 192·1—194·3 (direct), 198·2—199·9 (indirect), saponification number 203·5—204·7 (hot), 199·4—201·3 (cold), and iodine number 105·3—109·4.

Loangocopalolic acid, $C_{18}H_{34}O_2$, m. p. 60°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 185·1—187·3 (direct), 191·2—193·4 (indirect), saponification number 192·3—196·0 (hot), 199·1—200·2 (cold), and iodine number 88·7—88·1, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0·5% sodium hydroxide extracts *β-loangocopal resin*, $C_{23}H_{46}O_2$, m. p. 200°, which is insoluble in hot alcohol, and *loangocopalinic acid*, $C_{24}H_{44}O_2$, m. p. 165°, which is soluble in hot alcohol, and has acid number 146·2—148·7 (direct), 153·2—154·3 (indirect), saponification number 161·5—163·2 (cold), 166·7—168·9 (hot), and iodine number 70·2—71·6. C. S.

Sierra Leone Copal. M. WILLNER (*Arch. Pharm.*, 1910, **248**, 285—293).—Sierra Leone copal, acid number 108·6—114·4 (direct), 121·2—126·6 (indirect), saponification number 145·9—150·1 (hot), 142·8—146·7 (cold), dissolves completely in quinoline. In its examination it is extracted first by ether, which dissolves 63·4%, then by ether-alcohol, which dissolves the remainder with the exception of about 7%, the inorganic constituents of which contain sodium, potassium, calcium, magnesium, and silica.

The ethereal extract is treated successively with 0·5% ammonium carbonate, sodium carbonate, and 1% potassium hydroxide. From the crude acids isolated from the ammonium carbonate solution, *leonecopalic acid*, $C_{25}H_{48}O_3$, m. p. about 142°, has been obtained as an amorphous powder; it has acid number 136·4—138·0 (direct), 142·3—144·2 (indirect), saponification number 150·6—151·5 (hot), 154·0—155·7 (cold), and iodine number 64·8—65·2, and forms a lead salt which is insoluble in alcohol. *Leonecopalolic acid*, $C_{21}H_{38}O_2$, m. p. about 133°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 157·9—159·6 (direct), 164·4—165·2 (indirect), saponification number 171·4—173·0 (hot), 176·7—178·6 (cold), and

iodine number 76·7—79·6, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0·1% sodium hydroxide extracts *leonecopalinic acid*, $C_{14}H_{24}O_2$, m. p. about 184°, which has acid number 187·9—190·1 (direct), 194·0—195·5 (indirect), saponification number 205·5—207·5 (hot), 202·2—206·6 (cold), iodine number 110·0—111·7, and forms a lead salt soluble in alcohol, and *β-leonecopal resin*, $C_{14}H_{26}O_2$, m. p. about 195°, a white, amorphous powder insoluble in ether. C. S.

Glucoside of Ecballium elaterium. ARMAND BERG (*Bull. Soc. chim.*, 1910, [iv], 7, 385—388).—The author has stated previously (Abstr., 1898, ii, 447) that elaterin exists in fruit of the squirting cucumber for the most part, if not entirely, in the form of an amorphous, yellow glucoside, $C_{34}H_{48}O_{12}$, which is decomposed by a specific enzyme, elaterase, also occurring in the fruit, yielding elaterin and dextrose. Power and Moore (Trans., 1909, **95**, 1985) were unable to confirm the existence of this glucoside. The author has therefore repeated his experiments, and has confirmed his previous results. When boiled with dilute sulphuric acid the glucoside is hydrolysed, yielding acetic acid, dextrose, and a resinous product, probably consisting of anhydroelateridin with some impurity (compare Hemmelmayr, Abstr., 1906, i, 973). T. A. H.

Action of Silver Oxide on Elaterin. ARMAND BERG (*Compt. rend.*, 1910, **150**, 981—983).—Dry silver oxide is without action on elaterin; in presence of water, however, it brings about simultaneous oxidation and hydrolysis. The chief product is an amorphous, yellow substance, *elateridoquinone*, $C_{26}H_{36}O_7$, which is insoluble in alkalis, and does not develop a coloration with ferric chloride. The yellow colour is discharged by hydrochloric acid. Acetic acid, together with small quantities of a phenolic compound and an acid of unknown composition, have also been recognised amongst the products of the reaction. With elateridin, silver oxide yields traces of a substance insoluble in alkalis.

These observations throw doubt on the view that elaterin is an aldehydic compound. W. O. W.

Chlorophyll. IX. Oxidation of Chlorophyll Derivatives. RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Annalen*, 1910, **373**, 227—238. Compare this vol., i, 126).—Phylloporphyrin, pyrroporphyrin, rhodoporphyrin, and phytochlorin, when oxidised with lead dioxide and sulphuric acid, chromic acid, or Caro's acid, yield hæmatic acid and methylethylmaleinimide (compare Küster, Abstr., 1901, i, 58, 298; 1906, i, 337), together with smaller decomposition products, such as acetic acid and carbon dioxide. The quantities of hæmatic acid and methylethylmaleinimide formed have been carefully estimated, with the result that one mol. of a porphyrin derived from chlorophyll is found to yield 1 mol. of hæmatic acid and 2 mols. of methylethylmalein-

imide. Since hæmin when oxidised probably yields only 2 mols. of hæmatic acid (compare Küster, *loc. cit.*; Piloty, Abstr., 1909, i, 539), and does not yield methylethylmaleinimide, it follows that at least two of the four pyrrole nuclei in hæmin are different from those in the porphyrins derived from chlorophyll. W. H. G.

Determination of the Constitution of the Coumaran Ketones. CHARLES MARSCHALK (*Ber.*, 1910, **43**, 1695—1700. Compare Abstr., 1907, i, 950).—A direct proof of the constitution of the coumaran ketones was sought in the opening of the oxygen ring, but this does not readily take place. Coumaran, after heating with hydriodic acid, has the ring opened, forming *o*-ethylphenol, but 2-phenylcoumaran behaves altogether differently. It is now shown that benzylcoumaran, after heating with hydrogen iodide and subsequent treatment with alcoholic hydrogen chloride and zinc dust, forms *benzyl-*o*-ethylphenol*, $CH_2Ph{\cdot}C_6H_3Et{\cdot}OH$, a colourless oil, b. p. 323°/718 mm. By the action of methyl sulphate this is converted into p-*benzyl-*o*-ethylanisole*, $CH_2Ph{\cdot}C_6H_3Et{\cdot}OMe$, a colourless oil, b. p. 308—312°/720 mm., $n = 1{\cdot}566$. This constitution was established by the synthesis of the compound from *o*-ethylanisole, which was converted into the *p*-benzoyl derivative, and this reduced with sodium and alcohol to *p*-benzyl-*o*-ethylanisole. It is, therefore, established that on coupling aromatic acid chlorides with coumaran, the acid residue enters in the para-position (4) to the bridge carbon atom. E. F. A.

Preparation of Thionaphthen Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 221465).—When compounds having the general formula $R{<}^{S\cdot CH=CH\cdot S}_{CO_2R_1\ \ R_1O_2C}{>}R$, where R is a substituted benzene or naphthalene residue, R_1 a metal, alkyl or aryl group, are heated in the presence of alkalis or alkyloxides, either with or without the addition of such reducing agents as zinc, iron or sodium hyposulphite, they yield substantive dyes of the thionaphthen series.

3-*Oxy*-(1)-*thiosalicylic acid* is prepared by heating an intimate mixture of acetylene bis-*o*-thiolbenzoic acid and sodium hydroxide during half an hour at 220—230°, whilst the corresponding naphthalene derivative is similarly prepared from acetylene-bis-1-thiol-2-naphthoic acid. F. M. G. M.

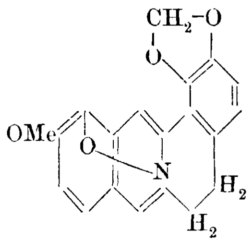
Agmatine. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1910, **66**, 257—251).—Agmatine, $C_5H_{14}N_4$, is a base which can be obtained from herring spawn after treatment with sulphuric acid at 4 atmospheres pressure in the autoclave. It was finally obtained as a crystalline aurichloride, or sulphate, and analysed. It is formed from arginine, and differs from it by CO_2. This is shown in the following formulæ:

$NH_2{\cdot}C(NH){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ arginine.
$NH_2{\cdot}C(NH){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ agmatine.

W. D. H.

Berberine. I. Berberrubine. GUSTAV FRERICHS (*Arch. Pharm.*, 1910, **248**, 276—284).—*Berberrubine*, $C_{19}H_{15}O_4N$, m. p. about 285°, is obtained by heating a mixture of berberine hydrochloride and carb-

amide for half an hour at 200°, pouring the partially cooled mass into water, and extracting with chloroform; the crude base obtained by the evaporation of the chloroform is purified through the hydrochloride. The pure base separates from water in dark red leaflets and flat needles containing $3H_2O$; the anhydrous substance is almost black, and has an extraordinary power of absorbing water. Berberine hydriodide is obtained by the addition of methyl iodide to berberrubine, which behaves like an internal phenoxide of the annexed constitution, assuming that the elimination of methyl alcohol from berberine occurs at the nearest methoxyl group.



The basic character of berberrubine is not great; it forms yellow, crystalline salts with strong acids, of which the *hydrochloride* and the *sulphate* are described; these are easily decomposed by alkali hydroxides or carbonates, or by ammonium hydroxide. The base is reduced to colourless *tetrahydroberberrubine*, $C_{19}H_{19}O_4N$, m. p. 167—168°, by zinc in the presence of sulphuric and acetic acids.

C. S.

The Alkaloid of Pseudocinchona africana. Hydrolysis by Alkalis. ERNEST FOURNEAU (*Compt. rend.*, 1910, **150**, 976—978. Compare Abstr., 1909, i, 600).—The new alkaloid recently obtained from the bark of *Pseudocinchona africana* closely resembles yohimbine except in its optical rotatory power. Sodium ethoxide in alcoholic solution converts it into an *acid*, $C_{20}H_{24}O_3N_2$, isomeric with the compound obtained in the same way from yohimbine (Spiegel, Abstr., 1903, i, 274). This substance crystallises from alcohol in slender, brilliant needles, m. p. below 300°, and is obtained in a hydrated form when precipitated by acids from its solutions in alkalis. The *silver* salt, $C_{20}H_{23}O_7N_2Ag,H_2O$, is a yellow powder.

W. O. W.

Corycavine. G. OTTO GAEBEL (*Arch. Pharm.*, 1910, **248**, 207—250).—In addition to the twelve alkaloids which have already been isolated from the rhizomes of *Corydalis cava*, the author has obtained a small amount of yet another *alkaloid*, $C_{25}H_{25}O_7N$ (?), m. p. 193—194°, $[\alpha]_D$ 100° in chloroform, the *hydrobromide* of which decomposes at 224°.

It is noteworthy that protopine has never been isolated from *Corydalis cava*, although it is present in almost all other species of the Papaveraceæ, and is regarded by Schmidt as the parent of the other Papaveraceæ alkaloids.

Having at his disposal a large quantity of crude material, the author has worked up 50 grams of crude corycavine, which is finally purified by crystallisation from hot alcohol-chloroform; the mother liquor contains the new alkaloid, m. p. 193—194°.

Most of the physical and the chemical properties of corycavine recorded by previous investigators are confirmed by the author; the m. p. is given as 218—219°, and the *aurichloride*, $C_{23}H_{23}O_6N,HAuCl_4$, has m. p. 178—179° (decomp.). The absence of hydroxyl and of

methoxy-groups is confirmed. The presence of at least one methylenedioxy-group is proved by Weber and Tollens' process. The nitrogen is monomethylated, and is present as tervalent nitrogen in a monocyclic system, as is proved, not only quantitatively by Herzig and Meyer's method of estimating methylimino-groups, but also by the behaviour of corycavine methiodide, which, submitted to Hofmann's process of exhaustive methylation, yields successively corycavinemethine, corycavinemethine methiodide, and a non-nitrogenous, amorphous substance and trimethylamine. *Corycavinemethine*, $C_{24}H_{25}O_6N$, m. p. 153—154°, is obtained by heating corycavine methiodide with a large excess of concentrated sodium hydroxide. It separates from alcohol in white needles, develops with concentrated hydrochloric acid an intense brown, then green, and finally deep blue coloration, decolorises bromine, and yields by heating with methyl iodide, *corycavinemethine methiodide*, $C_{25}H_{28}O_6NI$, m. p. 218—219° (decomp.), which is converted by distillation with concentrated sodium hydroxide into trimethylamine and an amorphous *substance*, which does not contain nitrogen and is practically insoluble in the usual organic solvents.

Corycavine, suspended in 100 times the quantity of water, and submitted for five to six days to reduction by hydrochloric acid and zinc dust at the temperature of boiling water, yields a mixture of two bases which partly remain in the liquid and partly separate as zincichlorides. One of the bases, which is soluble in ether, is a tertiary *base*, $C_{22}H_{25}O_4N$ (?), m. p. 125°, which forms well crystallised salts, contains a methylenedioxy-group, has a molecular weight of 368 by the ebullioscopic method in chloroform and also by the analysis of the *aurichloride*, and is probably formed at the expense of a methylenedioxy-group in corycavine, which therefore contains at least two such groups. The other base, the salts of which are not decomposed by ammonium hydroxide, is isolated by treating the hot aqueous solution of the zincichlorides (or the original mother liquor) with ammonium hydroxide, extracting the soluble base with ether, filtering the aqueous solution, acidifying it with acetic acid, and treating it with concentrated potassium iodide, whereby the *hydriodide* is precipitated. The *bromide*, *nitrate*, and *aurichloride*, m. p. about 185° (decomp.), are described. The pure base has not been analysed, but the intensely bitter taste of its salts, their stability to alkalis, and the formation of a new tertiary base by boiling the chloride with sodium hydroxide, indicate that the base is a quaternary ammonium hydroxide or a betaine thereof.

The oxidation of corycavinemethine in acetone at 0° by potassium permanganate yields, in addition to a small quantity of a *base*, m. p. 195—196°, an *acid*, $C_{18}H_{15}O_7N$, m. p. 110—111° (decomp.), which is apparently monocarboxylic. C. S.

Papaverine and Cryptopine. Amé Pictet and G. H. Kramers (*Ber.*, 1910, **43**, 1329—1335).—Commercial papaverine shows a characteristic deep bluish-violet coloration with cold concentrated sulphuric acid, and gives more or less characteristic colorations with other alkaloid reagents. Synthetical papaverine, however, gives none of

these colorations. Commercial papaverine can be readily purified by means of the acid oxalate, $C_{20}H_{21}O_4N,H_2C_2O_4$, which crystallises in stellar aggregates of needles, m. p. 196°. The papaverine obtained from this by means of sodium hydroxide no longer gives the colour reactions which are due to admixture to the extent of 4% with another alkaloid, cryptopine (compare T. and H. Smith, *Pharm. J.*, 1867, [ii], 8, 595, 716; Hesse, this Journ., 1871, 1065).

Cryptopine crystallises in hexagonal prisms or plates, m. p. 218°. The dichromate forms minute, yellow prisms; the *picrate* forms long needles, grouped like a paint-brush, m. p. 215°; the *mercurichloride* is colourless, m. p. 185°; the *aurichloride* crystallises in brownish-yellow needles, which blacken at 200°, m. p. 205°; the *platinichloride* forms yellow, concentrically-grouped needles, m. p. 204° (decomp.).

Cryptopine is a saturated base, and is not attacked by hydrogen; the stannichloride crystallises in needles, m. p. 190° (decomp.). It contains two methoxyl groups and one methyl attached to nitrogen. It probably contains the methylenedioxy-group, $CH_2<^{O-}_{O-}$, as it gives a green coloration and the characteristic absorption spectrum with sulphuric and gallic acids. It contains neither phenol nor alcoholic hydroxyl, nor a keto-group. E. F. A.

Compound of Acetylbromoglucose and Pyridine. EMIL FISCHER and KARL RASKE (*Ber.*, 1910, **43**, 1750—1753).—Analogous to chlorodimethyl ether, β-acetylbromoglucose combines with pyridine to form *tetra-acetylglucosepyridinium bromide.* This crystallises in colourless, obliquely-cut prisms, m. p. 174° (corr.), $[\alpha]_D^{20}$ $-6{\cdot}43°$ ($\pm 0{\cdot}2°$). The crystallisation is greatly facilitated by the addition of a little phenol to the reaction mixture. The aqueous solution is neutral towards litmus, and reduces Fehling's solution only very feebly. When shaken with silver oxide, the free *base* is obtained, and remains as a syrup on evaporation. The only sparingly soluble salt is the *hydrogen ferrocyanide*, crystallising in stellar aggregates or bunches of needles, which are at first faintly yellowish-green, but become blue after a time or on crystallisation from hot water.

In addition to the crystalline tetra-acetylglucosepyridinium bromide, an amorphous, probably stereoisomeric, product of different rotation is obtained. E. F. A.

Salts of a Hexa-acetatotripyridinetrichromi-Base. RUDOLF F. WEINLAND and ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1910, **67**, 167—182).—When pyridine is added to a concentrated solution of hexa-acetatotrichromic diacetate (Weinland and Dinkelacker, Abstr., 1909, i, 757) and the solution is warmed, the diacetate of a new base containing 3 mols. of pyridine is obtained. The mother liquor contains a basic acetate, $Cr_3(OAc)_3(OH)_3,9H_2O$, which will be described in a further communication.

The diacetate is obtained free from the accompanying pyridine acetate by precipitating with sodium acetate, and serves for the preparation of the other salts. All of these contain six acetic residues, whatever be the conditions of preparation, and these residues are therefore considered to form part of the cation complex.

The salts with colourless acids are pale green, but concentrated solutions are dark red, becoming pale green on dilution. Some of the salts are very sparingly soluble. The secondary and tertiary salts have an acid reaction, but the primary salts are neutral. The base may be prepared by the action of silver oxide on the iodide, and forms an unstable, alkaline solution.

Hexa-acetatotripyridinetrichromic triacetate,

$$\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH_2)_2}\end{matrix}\right]\mathrm{OAc_3,7H_2O},$$

prepared by precipitating the crude acetate with sodium acetate and acetic acid, forms small, green needles, readily soluble in water. The mono- and di-acetates were not completely separated. The *iodide*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH)_2}\end{matrix}\right]\mathrm{I}$, prepared by precipitation of the acetate solution with potassium iodide, forms almost insoluble, very pale green crystals. The *chloride-acetate*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{OH_2}\\ \mathrm{OH}\end{matrix}\right]\begin{matrix}\mathrm{Cl}\\ \mathrm{OAc}\end{matrix}\mathrm{,6H_2O}$, is precipitated by an excess of sodium chloride. The *nitrate*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH)_2}\end{matrix}\right]\mathrm{NO_3,5H_2O}$, is very sparingly soluble, one part dissolving in 216·9 parts of water. The *nitrate-acetate*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{OH_2}\\ \mathrm{OH}\end{matrix}\right]\begin{matrix}\mathrm{NO_3}\\ \mathrm{OAc}\end{matrix}\mathrm{,3H_2O}$; the *platinichloride*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH)_2}\end{matrix}\right]\frac{1}{2}\mathrm{PtCl_6}$; the *stannichloride*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{OH_2}\\ \mathrm{OH}\end{matrix}\right]\mathrm{SnCl_6,7H_2O}$; the *permanganate*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH)_2}\end{matrix}\right]\mathrm{MnO_4,H_2O}$; the *ferricyanide*,

$$\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3Py}\\ \mathrm{(OH)_2}\end{matrix}\right]\mathrm{Fe(CN)_6,9H_2O},$$

and the *chromate* have been analysed. A number of other salts are briefly described.

[With E. BÜTTNER.]—Ammonia may also be introduced, by passing the gas into an alcoholic solution of hexa-acetatotrichromic diacetate. The sparingly soluble *hexa-acetatotriammine-trichromic iodide*,

$$\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{3NH_3}\\ \mathrm{(OH)_2}\end{matrix}\right]\mathrm{I},$$

resembles the pyridine compound. C. H. D.

Course of the Friedel-Craft Reaction with Unsymmetrical Polycarboxylic Acids. II. ALFRED KIRPAL (*Monatsh.*, 1910, **31**, 295—299. Compare Abstr., 1909, i, 509).—Unlike the case of

cinchomeronic anhydride (*loc. cit.*), the addition of benzene to quinolinic anhydride in the presence of aluminium chloride yields only one product, namely, 3-benzoylpicolinic acid in 92% yield. The other product, 2-*benzoylnicotinic acid*, $C_5NH_3Bz\cdot CO_2H$, m. p. 176°, which is not formed or only in inappreciable amount in the preceding reaction, can be prepared from benzene, 3-methyl quinolinate-2-chloride and aluminium chloride. C. S.

New Trimethylenepyrrole Derivatives. II. MARIO GUIGLIENO (*Atti. R. Accad. Sci. Torino*, 1910, **45**, 449—468).—The hydrolysis of the α- and β-forms of 3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (compare this vol., i, 427) by 2 or more mols. of sodium hydroxide in dilute solution at the ordinary temperature consists of a reaction with $3H_2O$, two isomeric mono-amides of 3 : 5-dicarboxy-4-methyl-4-ethyltrimethylenedicarbonimides,

$$NH<\begin{matrix}CO\cdot C(CO\cdot NH_2) \\ CO\cdot C(CO_2H)\text{—}\end{matrix}>CMeEt,$$

being obtained.

The complete hydrolysis of the second cyanogen group to carboxyl is accomplished only with difficulty. It is hence evident that tertiary nitriles, which are usually regarded as hydrolysable with difficulty, can be very easily hydrolysed in certain cases. The influence of alkyl groups or negative radicles in hindering the hydrolysis of the cyanogen group is not general, or at any rate varies considerably according to the nature of the fundamental nucleus. The iminic group is perhaps more resistant to the action of alkali than is generally believed, and in some cases may exhibit very marked stability. Whilst the iminic hydrogen possesses a very feeble acid character when the neighbouring atoms or groups are neutral or nearly so, this character seems to be influenced regularly by the introduction of more active substituent groups, being increased by highly electronegative groups like cyanogen, and diminished to the vanishing point by the proximity of one or more acid groups.

The α-*amide*, $C_{10}H_{12}O_5N_2$, prepared from α-3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (m. p. 247—248°), forms colourless, rhombic prisms, m. p. 194° (decomp.) or 232—235° (Maquenne block). It behaves as a dibasic acid weaker than phenolphthalein; the *ammonium hydrogen*, *sodium*, and *silver* ($C_{10}H_{10}O_5N_2Ag_2,2H_2O$) salts were prepared.

The β-isomeride, $C_{10}H_{12}O_5N_2$, prepared from the corresponding trimethylenedicarbonimide derivative, forms shining crystals, m. p. 206° (decomp.), decomposes instantaneously on the Maquenne block at 280°. The *silver* salt, $C_{10}H_{10}O_5N_2Ag_2,2H_2O$, was prepared.

The *amide* of 3-*carboxy*-4-*methyl*-4-*ethyltrimethylenedicarbonimide*, $NH<\begin{matrix}CO\cdot CH\text{———} \\ CO\cdot C(CONH_2)\end{matrix}>CMeEt$, prepared by heating the α-mono-amide of the dicarboxy-acid (m. p. 194°) at 165—170°, forms shining crystals, m. p. 141—143° or 142—143° (Maquenne block), and has a feeble acidic character; its *silver* salt, $C_9H_{11}O_3N_2Ag$, was analysed.

The α-*dicarboxy-acid*, $NH<\begin{matrix}CO\cdot C(CO_2H) \\ CO\cdot C(CO_2H)\end{matrix}>CMeEt$, forms small, white

needles ($+2H_2O$), decomposing instantaneously on the Maquenne block at 182—183°, and is dibasic towards phenolphthalein, being the only compound of the series in which the iminic hydrogen of the pyrrole ring exhibits no acid reaction; the *sodium hydrogen* salt was analysed and various other salts prepared.

a-4-Methyl-4-ethyltrimethylenedicarbonimide, $NH<\begin{matrix}CO\cdot CH\\ CO\cdot CH\end{matrix}>CMeEt$, prepared by heating the above dicarboxy-acid, forms slender, nacreous laminæ, m. p. 61—63°, and exhibits extremely feeble acid properties; when its solution is neutralised, it gives precipitates with salts of the heavy metals. T. H. P.

Dihydro*iso*indole Bases. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 1353—1360. Compare Abstr., 1907, i, 960; 1909, i, 507).—A tertiary dihydro*iso*indole, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>NR$, was sought in which the alkyl residue R, in presence of cyanogen bromide, was less firmly attached to nitrogen than the xylyl residue of the ring. This xylyl residue is found to take up a position between benzyl and methyl in its attachment to nitrogen; accordingly in the case of *N*-methyl- and *N*-ethyl-dihydro*iso*indoles the ring is opened by cyanogen bromide. *N*-Benzyl-dihydro*iso*indole under the same conditions has the benzyl eliminated to some extent. *N*-Allyldihydro*iso*indole is transformed into *N*-cyano-dihydro*iso*indole.

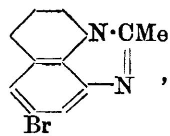
o-*Xylylmethylaniline*, prepared by the interaction of methyl-aniline and *o*-xylyl bromide, forms a clear liquid, b. p. 200°/35 mm., m. p. 34°; the picrate has m. p. 110°. It interacts with cyanogen bromide in sealed tubes at 100°, forming a mixture of phenyl-*o*-xylyl-cyanide, phenylmethylcyanamide, and ω bromo-*o*-xylene.

Benzyldihydro*iso*indole is a colourless oil, b. p. 185—186°/10 mm.; it reacts with cyanogen bromide, forming the *quaternary ammonium bromide*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N(C_7H_7)_2Br$, m. p. 220°. It also in part decomposes into benzyl bromide and N-*cyanodihydro*iso*indole*.

*Allyldihydro*iso*indole*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot C_3H_5$, prepared by the reaction of xylylene bromide and allylamine in chloroform solution, has b. p. 125°/17 mm. It forms an oily *picrate* and a methiodide, m. p. 131°. It reacts very energetically with cyanogen bromide, forming allyl-bromide and *cyanodihydro*iso*indole*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot CN$, which forms colourless crystals, m. p. 80—81°. Boiling for a short time with 25% sulphuric acid converts it into *dihydro*iso*indolecarboxylamide*, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>N\cdot CO\cdot NH_2$, m. p. 183°. Further hydrolysis yields dihydro*iso*indole, b. p. 213—214°, previously prepared synthetically by Gabriel (Abstr., 1893, i, 347). E. F. A.

Derivatives of Tetrahydroquinoline. II. FRANZ KUNCKELL [with W. THEOPOLD] (*Ber. deut. pharm. Ges.*, 1910, **20**, 214—225).—The work described in the first part of this research (this vol., i, 429) is continued, bromomethyltetrahydroquiniminazole, dibromotetrahydroquino-

line, dibromoquinoline, and some of their derivatives being described. It has been pointed out already (*loc. cit.*) that the end product of the reduction of 6-bromo-8-nitro-1-acetyltetrahydroquinoline is a bromo-anhydro-base of the class that Bamberger and Wulz have called "quiniminazoles" (*peri*-quinolineazoles) (Abstr., 1891, i, 1255). The reduction can be effected by tin and hydrochloric acid, as described already, or by means of zinc dust and acetic acid.

2-*Methyl*-8-*bromotetrahydroquinolineazole*, 

, m. p. 165°, separates from light petroleum in colourless crystals, and shows none of the characteristic properties of a tetrahydroquinoline derivative. The *hydrochloride*, m. p. 253°, obtained by the action of hydrogen chloride on an ethereal solution of the base, crystallises in faintly yellow needles. The *platinichloride*, m. p. above 300°, is a brown, amorphous product.

On bromination in acetic acid, tetrahydroquinoline furnishes 5 : 7-dibromotetrahydroquinoline hydrobromide, m. p. 185°, which forms colourless crystals, and on addition of alkali to its solution in warm water yields the dibromo-base as a yellow, non-volatile oil. The hydrochloride, m. p. 178°, forms colourless crystals, and the platinichloride, m. p. 210° (decomp.), crystallises in small, brown needles. This dibromotetrahydroquinoline is probably identical with that of Hoffmann and Königs (Abstr., 1883, 1145).

5 : 7-*Dibromo*-8-*nitroquinoline*, m. p. 180°, prepared from 8-nitroquinoline (Knüppel, Abstr., 1896, i, 391) by heating it at 130° with water and bromine (2 mols.), crystallises from alcohol in minute, almost colourless needles. It cannot be further nitrated, and the bromine atoms are not reactive. The substance is scarcely basic, but although it forms no hydrochloride, a brown, microcrystalline *platinichloride*, m. p. 265° (decomp.), can be obtained by adding platinum chloride solution, saturated with hydrogen chloride, to a solution of the substance in alcohol, also saturated with hydrogen chloride. On heating at 230° with alcohol, saturated with ammonia at 0°, 5 : 7-dibromo-8-nitroquinoline is converted into the corresponding dibromoaminoquinoline, m. p. 127°, already obtained by Claus and Ammelburg (Abstr., 1894, i, 553). The *acetyl* derivative of this has m. p. 172°, and the *benzoyl* derivative, m. p. 155—156°. 5-*Bromo*-8-*nitro*-6-*methylquinoline*, m. p. 185—186°, prepared by heating 8-nitro-6-methylquinoline (Knüppel, Abstr., 1896, i, 391) with bromine in a closed tube at 130°, forms small, colourless crystals from a mixture of alcohol, ether, and benzene. It does not furnish a hydrochloride, but gives a *platinichloride*; the bromine atom is not attacked by aqueous or alcoholic alkali at 250°.

T. A. H.

Derivatives of Benzothiazole. Emil Besthorn (*Ber.*, 1910, **43**, 1519—1526).—1-Imino-2-methylbenzothiazoline,

$$C_6H_4{<}^{NMe}_{S}{>}C{:}NH$$

(Hugershoff, Abstr., 1903, i, 866), obtained by the action of bromine on a chloroform solution of *as*-phenylmethylthiocarbamide, is identical with

Fischer and Besthorn's phenylmethylthiocarbizine. With nitrous acid it yields a *nitroso*-derivative, $C_6H_4<\genfrac{}{}{0pt}{}{NMe}{S}>C:N\cdot NO$, which crystallises in slender, yellow needles or compact, red crystals. When gently heated, it decomposes at about 147°, but when heated rapidly explodes at 152°. It reacts with concentrated hydrochloric acid, yielding nitrous fumes, and when its xylene solution is boiled, nitrogen is evolved and *2-methylbenzothiazolone*, $C_6H_4<\genfrac{}{}{0pt}{}{NMe}{S}>CO$, is formed. This compound crystallises from ether in compact prisms, m. p. 76°, and yields salts with concentrated mineral acids. It is decomposed when boiled with alcoholic potassium hydroxide solution, and does not yield a phenylhydrazone.

2-Methylbenzothiazolonehydrazone, $C_6H_4<\genfrac{}{}{0pt}{}{NMe}{S}>C:N\cdot NH_2$, obtained by reducing the nitroso-derivative with zinc dust and acetic acid at 15°, crystallises in colourless, thin plates, m. p. 143—144°, and has very feeble reducing properties at the ordinary temperature. Its *hydrochloride* is sparingly soluble in concentrated hydrochloric acid. The *benzylidene* derivative, $C_6H_4<\genfrac{}{}{0pt}{}{NMe}{S}>C:N\cdot N:CHPh$, forms pale yellow plates, m. p. 163°, has but feebly basic properties, and gives a characteristic blue coloration with ferric chloride and a few drops of hydrochloric acid in aqueous alcoholic solution. J. J. S.

Action of Alkalis on Aromatic Acid Hydrazides. THEODOR CURTIUS and HEINRICH MELSBACH [and, in part, RISSOM] (*J. pr. Chem.*, 1910, [ii], **81**, 501—551).—Curtius observed (Abstr., 1900, i, 701) that the action of dilute alkali on dextrose and benzoylhydrazine in aqueous solution at the ordinary temperature produced, not benzosazones, but benzoylbenzylidene hydrazine, the dextrose apparently playing no part in the reaction. The authors have now examined the reaction fully. A known quantity (about 3 mols.) of benzoylhydrazine is dissolved in a measured volume of water, and a definite amount of sodium hydroxide (1 mol.) is added; after a definite interval of time, the precipitated benzoylbenzylidenehydrazine is collected and weighed, its purity being checked by hydrolysing it by dilute sulphuric acid, distilling the benzaldehyde with steam into a solution of hydrazine sulphate, and collecting and weighing the benzylideneazine produced.

It is found that the presence of a small quantity of dextrose increases the yield of benzoylbenzylidenehydrazine; by increasing the amount of dextrose, the yield of the hydrazide is diminished. At 70° the yield of benzoylbenzylidenehydrazine is considerably less than at 40°, or at the ordinary temperature, but again the presence of dextrose exercises a favourable influence on the yield. When the amount of sodium hydroxide is increased to 3 mols., the authors find that in experiments in which dextrose is present the product during the first four weeks is benzoylbenzylidenehydrazine, and during the next four weeks, benzylideneazine; when dextrose is not present, the only product is the azine.

The conversion of benzoylhydrazine into benzoylbenzylidenehydrazine also occurs in the presence of ammonium hydroxide, or, very slowly, in

that of hydrazine hydrate. The change also takes place in alcoholic solution; in this solvent the best yield, 47·9%, of benzoylbenzylidenehydrazine is obtained; the rest of the benzoylhydrazine suffers hydrolysis, benzoic acid being produced.

The reaction is explained by the elimination of hydrazine from two molecules of benzoylhydrazine, which reduces one of the resulting residues, whereby benzoylbenzylidenehydrazine is formed:

$$2NHBz{\cdot}NH_2 \longrightarrow N_2H_4 + 2{\cdot}NHBz \longrightarrow {\cdot}NHBz + {\cdot}N{:}CHPh \longrightarrow NHBz{\cdot}N{:}CHPh.$$

The hydrolysis of the last by water (2 mols.) yields benzoic acid, benzaldehyde, and hydrazine, from the last two of which benzylideneazine is produced.

The reaction represented by the scheme:

$$C_6H_4R{\cdot}CO{\cdot}NH{\cdot}NH_2 \longrightarrow C_6H_4R{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4R$$

has been examined in the case of other aromatic acid hydrazides. It is found that in aqueous or alcoholic solution in the presence of sodium hydroxide the conversion takes place when R is *m*-NO_2 *m*-Cl, *p*-Br, *p*-Me, *o*-NH_2, *o*-OH, or *p*-OMe, but not when R is *o*-NO_2 or *p*-NO_2.

The following new compounds are described: o-*Nitrobenzoyl*-o-*nitrobenzylidenehydrazine*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, m. p. 215°; the para-*isomeride*, m. p. 274°; the meta-*isomeride*, m. p. 248°; p-*bromobenzoyl*-p-*bromobenzylidenehydrazine*, m. p. 232—233°; p-*bromobenzylideneazine*, m. p. 209·5—210°; m-*chlorobenzoyl*-m-*chlorobenzylidenehydrazine*, m. p. 147—148°; m-*chlorobenzylideneazine*, m. p. 143—144°: o-*aminobenzoyl*-o-*aminobenzylidenehydrazine*, m. p. 188—189°; o-*hydroxybenzoyl*-o-*hydroxybenzylidenehydrazine*, m. p. 277°; *anisoylhydrazine*, m. p. 136°; *anisoylanisylidenehydrazine*, m. p. 171°. C. S.

Relations between Constitution and Phototropy. Maurice Padoa and F. Graziani (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 489—495).—The relationship between constitution and phototropy observed with the tolyl- and naphthyl-hydrazones (Abstr., 1909, i, 964; this vol., i, 135) is found to hold also with the xylylhydrazones; thus, the xylylhydrazine in which $Me{:}Me{:}N_2H_3 = 1:3:4$ yields non-phototropic hydrazones, whilst when $Me{:}Me{:}N_2H_3 = 1:2:4$ the hydrazones are, in nearly all cases, phototropic.

Benzaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2{\cdot}N_2H{:}CHPh$, forms shining, yellow scales, m. p. 86°, undergoes alteration in the air, and is not phototropic.

Anisaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}OMe$, forms slender, yellow needles, m. p. 97°, changes in the air, and does not exhibit phototropy.

Cinnamaldehyde-1:3:4-*xylylhydrazone*, $C_6H_3Me_2{\cdot}N_2H{:}CH{\cdot}CH{:}CHPh$, forms lemon-yellow, non-phototropic crystals, m. p. 115°.

Cuminaldehyde-1:3:4-*xylylhydrazone*,

$$C_6H_3Me_2{\cdot}N_2H{:}CH{\cdot}C_6H_4{\cdot}CHMe_2,$$

forms white needles, m. p. 76°, and is not phototropic.

Piperonaldehyde-1:3:4-*xylylhydrazone*,

$$C_6H_3Me_2{\cdot}N_2H{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2,$$

forms faintly red, non-phototropic crystals, m. p. 90°.

p-*Tolualdehyde*-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4Me,$$

forms canary-yellow crystals, m. p. 99°, and is not phototropic.

Vanillin-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_3(OH)\cdot OMe,$$

crystallises in slender, yellow, non-phototropic crystals, m. p. 99°.

Salicylaldehyde-1 : 3 : 4-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4\cdot OH,$$

forms yellow needles, m. p. 86°, and is non-phototropic.

1 : 2 : 4-*Xylylhydrazine*, $NH_2\cdot NH\cdot C_6H_3Me_2$, forms yellowish-white needles, m. p. 57°, and its *hydrochloride*, shining, white scales, m. p. 197° (decomp.).

Benzaldehyde-1 : 2 : 4-*xylylhydrazone* forms a faintly yellow, crystalline powder, m. p. 126°, and exhibits phototropy.

Anisaldehyde-1 : 2 : 4-*xylylhydrazone* crystallises in white, phototropic needles, m. p. 116°.

Cinnamaldehyde-1 : 2 : 4-*xylylhydrazone* forms yellow needles, m. p. 153°, and is non-phototropic.

Cuminaldehyde-1 : 2 : 4-*xylylhydrazone* forms slender, yellow needles, m. p. 143°, and exhibits phototropy.

Piperonaldehyde-1 : 2 : 4-*xylylhydrazone* crystallises as a white, phototropic powder, m. p. 118°.

p-*Tolualdehyde*-1 · 2 : 4-*xylylhydrazone* forms a canary-yellow, crystalline powder, m. p. 135°, and is phototropic.

Vanillin-1 : 2 : 4-*xylylhydrazone* forms a white, crystalline, non-phototropic powder, m. p. 118°.

Salicylaldehyde-1 : 2 : 4-*xylylhydrazone* forms yellowish, faintly phototropic needles, m. p. 157°.

Piperonaldehyde-β-naphthylhydrazone (compare Rothenfusser, Abstr., 1908, i, 52) and vanillin-β-naphthylhydrazone, m. p. 185° (Rothenfusser, *loc. cit.*, gave 187°) are phototropic.

p-*Tolualdehyde* - β - *naphthylhydrazone*, $C_{10}H_7\cdot N_2H\colon CH\cdot C_6H_4Me$, crystallises in faintly yellow, phototropic scales, m. p. 188°.

Salicylaldehyde - β - *naphthylhydrazone*, $C_{10}H_7\cdot N_2H\colon CH\cdot C_6H_4\cdot OH$, forms dirty-yellow needles, m. p. 187°, and is non-phototropic.

T. H. P.

Isatinanils. II. Derivatives of Thionaphthenquinone. RUDOLF PUMMERER (*Ber.*, 1910, **43**, 1370—1376. Compare this vol., i, 77).—The methylene group of 3-hydroxy-1-thionaphthen reacts even more smoothly than that of indoxyl with alcoholic solutions of aromatic nitroso-compounds in the presence of sodium hydroxide, thionaphthenquinone-2-anils being formed in good yield, together with a very small amount of "thioindigo." In this way thionaphthenquinone-2-anil is obtained from nitrosobenzene; *thionaphthenquinone*-p-*dimethylamino-2-anil*, $C_6H_4{<}{}^{S}_{CO}{>}C\colon N\cdot C_6H_4\cdot NMe_2$, m. p. 176°, from *p*-nitrosodimethylaniline; 5-*methylthionaphthenquinone*-p-*dimethylamino-2-anil*, m. p. 200°, from 3-hydroxy-5-methyl-1-thionaphthen; 5-*chlorothionaphthenquinone*-p-*dimethylamino-2-anil*, m. p. 148—149°, and 7-*chlorothionaphthenquinone*-p-*dimethylamino-2-anil*, m. p. 147°, from the corre-

sponding chlorinated hydroxythionaphthens; and *thionaphthenquinone*-p-*phenylamino*-2-*anil*, m. p. 193°, from *p*-nitrosodiphenylamine.

The anil group in these compounds is very loosely held. They are decomposed by mineral acids, yielding the corresponding thionaphthenquinones, and react with substances containing a reactive methylene group, such as indoxyl, oxindole, 3-hydroxy-1-thionaphthen, or acenaphthenone, forming an indigoid dye, the anil group being eliminated as arylamine.

The salts of these anils are of interest. Isatin-*p*-dimethylamino-2-anil forms a hydrate, a yellow hydrochloride, and also an isomeric blue hydrochloride (*loc. cit.*). The latter salt may be quinonoid, but in any explanation of the isomerism a possible migration of the indole-iminic hydrogen atom must not be overlooked. Such a contingency is impossible in the case of the thionaphthenquinoneanils. Thionaphthenquinone-*p*-dimethylamino-2-anil forms a yellow *hydrochloride*, but no hydrate, whilst thionaphthenquinone-*p*-phenylamino-2-anil forms a green *hydrate*, containing H_2O, and a hydrated blue *hydrochloride*, $C_{20}H_{14}ON_2S,1\frac{1}{2}HCl,1\frac{1}{2}H_2O$, decomposing at 120°. These facts alone do not elucidate the constitution of the blue salts, but it is noteworthy that the formation of blue salts runs pari passu with hydrate formation.

Thionaphthenquinone-2-oxime also is hydrolysed by boiling strong mineral acids, yielding thionaphthenquinone, and reacts with indoxyl in dilute acetic or weak mineral acid solution forming indigotin and 2′-indoxyl-2-thionaphthen-2′-one. C. S.

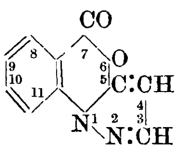
Isatinanils. III. Leuco-compounds. RUDOLF PUMMERER and MAXIMILIAN GÖTTLER (*Ber.*, 1910, 43, 1376—1386. Compare preceding abstract).—*Isatin-leuco-3-anil*, $C_{14}H_{12}ON_2$, m. p. 192° in an atmosphere of carbon dioxide, is obtained by reducing isatin-3-anil in 2% sodium hydroxide by sodium hyposulphite and liberating the leucoanil by sodium hydrogen carbonate in an atmosphere of coal gas. It separates from benzene in colourless prisms.

Isatin-leuco-2-anil, $C_6H_4<\substack{CO\\NH}>CH\cdot NHPh$, m. p. 115—116°, is prepared by reducing an alcoholic solution of isatin-2-anil by a solution of sodium hyposulphite in 4% sodium hydroxide and alcohol in an atmosphere of coal gas, and decomposing the product by sodium hydrogen carbonate; it crystallises in citron-yellow prisms, and oxidises to the anil with extreme readiness. *Isatin*-p-*dimethylamino-leuco-2-anil*, $C_{16}H_{17}ON_3$, m. p. 150—155°, obtained in a similar manner, is colourless, and is less readily oxidised than the preceding anil. Isatin-leuco-2-anil behaves in a remarkable manner with acids, concentrated sulphuric acid, dilute hydrochloric acid, hot or cold, acetic acid, or even a 1·5% boiling solution of benzoic acid, causing two simultaneous reactions, by one of which aniline and indigotin are produced, whilst the other results in the formation of aniline, water, and indirubin-2-anil. Isatin-leuco-2-anil is reduced extremely slowly by alkaline sodium hyposulphite, fairly rapidly to indoxyl by cold ammonium sulphide, and instantly to indigotin by warm ammonium sulphide in an atmosphere of carbon dioxide. Isatin-2-anil, however,

is instantly reduced to indoxyl by ammonium sulphide at 0° in an atmosphere of carbon dioxide.

Indirubin-2-anil, $C_6H_4<{NH \atop CO}>C:C<{-C_6H_4- \atop C(:NPh)}>NH$, m. p. 219—220°, can be obtained by the interaction of isatin-leuco-2-anil and a hot alkaline solution of indoxyl (indoxylic acid), but is best prepared by slowly adding a hot alcoholic solution of isatin-2-anil to a hot aqueous-alcoholic alkaline (0·5% sodium hydroxide) solution of indoxylic acid in an atmosphere of coal gas. It separates from benzene in metallic, violet plates containing C_6H_6, forms a blue *hydrochloride*, $C_{22}H_{15}ON_3,CHl$, m. p. 245°, and yields isatin and isatin-2-anil by oxidation by potassium permanganate in glacial acetic acid. C. S.

Anhydrides of 1-Phenyl-5- and -*o*-3-pyrazolonecarboxylic Acids. AUGUST MICHAELIS (*Annalen*, 1910, **373**, 129—212).—The present communication contains an account of the preparation and properties of several derivatives of a compound having the annexed constitution, which it is proposed to designate pyrazo*iso*coumarazone, since it is formed by the union of a pyrazole ring with the *iso*coumarazone nucleus (compare Cebrian, Abstr., 1898, i, 582); the anhydride of 1-phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid, formed by the elimination of hydrogen chloride from 5-chloro-1-phenyl-3-methylpyrazole-2′-carboxylic acid (compare Michaelis and Eisenschmidt, Abstr., 1904, i, 624), is to be regarded, therefore, as 3-methylpyrazo*iso*coumarazone. This compound has been isolated in three isomeric modifications; the γ-isomeride is formed by the distillation of 5-chloro-1-phenyl-3-methylpyrazole-2′-carboxylic acid, and passes into the α-isomeride when heated with zinc chloride or water for some time, and into the β-isomeride when acted on by nitric or sulphuric acid or when distilled under the atmospheric pressure. 1-Phenyl-3-methyl-5-pyrazolone-2′-carboxylic acid is obtained when hydrochloric acid is added to a solution of any one of the isomerides in alkali; similarly, the same salt, $C_{11}H_8O_2N_2,HCl,H_2O$, is formed by heating the three modifications with an excess of hydrochloric acid, yet the isomerism is not merely physical, since three isomeric 4-bromo-derivatives are formed by acting on the isomerides with bromine in glacial acetic acid.



The β-isomeride has also been prepared by the condensation of ethyl acetoacetate with *o*-hydrazinobenzoic acid.

The parent substance, namely, pyrazo*iso*coumarazone, has been similarly prepared from 5-chloro-1-phenylpyrazole-2′-carboxylic acid, also the 3-phenyl derivative from 5-chloro-1 : 3-diphenylpyrazole-2′-carboxylic acid, and by the condensation of ethyl benzoylacetate with *o*-hydrazinobenzoic acid; isomeric forms of these compounds have not been isolated. The pyrazo*iso*coumarazones resemble *iso*coumarin and phthalic anhydride in their general chemical behaviour.

3-Chloro-1-phenyl-5-methylpyrazole-2′-carboxylic acid, when heated, also loses hydrogen chloride, yielding methylbenzo*bis*pyrazolone, $\begin{matrix} C_6H_4\cdot N\cdot CMe \\ CO—N\cdot CO \end{matrix}>CH$ (compare Michaelis and Reinighaus, Abstr., 1909,

i, 530), but the halogen of 4-bromo-1-phenyl-3-methylpyrazole-2′-carboxylic acid is not eliminated as hydrogen bromide by heating the acid.

[With Max Ziesel.]—*Ethyl* o-*tolylhydrazinomethylenemalonate*, $C_6H_4Me\cdot NH\cdot NH\cdot CH{:}C(CO_2Et)_2$, is prepared by the interaction of *o*-tolylhydrazine with ethyl ethoxymethylenemalonate; it forms colourless, rhombic plates and prisms, m. p. 110°, and is converted by aqueous sodium hydroxide into 1-o-*tolyl*-5-*pyrazolone*, $C_{10}H_{10}ON_2$, which crystallises in colourless prisms and plates, m. p. 177°, and when heated with phosphorus oxychloride yields 5-*chloro*-1-o-*tolylpyrazole*, $C_{10}H_9N_2Cl$, a colourless liquid with a characteristic odour; the latter substance, when oxidised with chromic acid, yields 5-*chloro*-1-*phenylpyrazole*-2′-*carboxylic acid*, $C_{10}H_7O_2N_2Cl$, which crystallises in long, colourless needles, m. p. 125°, and on distillation yields *pyrazo*iso*coumarazone*, colourless needles, m. p. 116°, b. p. 308°. The latter substance is converted (1) by bromine into 4-*bromopyrazo*iso*coumarazone*, $C_{10}H_5O_2N_2Br$, slender, colourless needles, m. p. 199°, and (2) by aqueous ammonia under pressure at 120° into 7-*hydroxypyrazoquinazoline*, $OH\cdot C\left\langle\begin{matrix} N{-}{-}{-}{-}C{:}CH \\ C_6H_4\cdot N{-}N \end{matrix}\right\rangle CH$, which forms small, colourless needles, m. p. 265°, and is converted by phosphoryl chloride into 7-*chloropyrazoquinazoline*, $C_{10}H_6N_3Cl$, pale yellow needles, m. p. 130°.

[With Carl Krug, Julius Leo, and Max Ziesel.]—The o-*carboxyphenylhydrazone* of ethyl acetoacetate,

$$CO_2Et\cdot CH_2\cdot CMe{:}N\cdot NH\cdot C_6H_4\cdot CO_2H,$$

prepared by the action of *o*-hydrazinobenzoic acid on ethyl acetoacetate, forms slender, yellow needles, m. p. 125°, and is converted when distilled (1) under a pressure of 15 mm. into β-3-*methylpyrazo*iso*coumarazone*, white needles, m. p. 132°, and (2) under the atmospheric pressure into γ-3-*methylpyrazo*iso*coumarazone*, white needles, m. p. 112°, b. p. 345°; α-3-*methylpyrazo*iso*coumarazone* crystallises in white needles, m. p. 165°. The isomeric 3-methylpyrazo*iso*coumarazones, when acted on by a solution of bromine in glacial acetic acid, yield the corresponding 4-*bromo*-3-*methylpyrazo*iso*coumarazones*, $C_{11}H_7O_9N_2Br$; the α-compound forms yellow needles, m. p. 187°; the β-isomeride crystallises in colourless needles, m. p. 151°; the γ-modification forms colourless needles, m. p. 135—137°, and is converted by repeated crystallisation from alcohol into the β-isomeride. The β- and γ-isomeric forms of 3-methylpyrazo*iso*coumarazone, when treated with iodine in glacial acetic acid, yield γ-4-*iodo*-3-*methylpyrazo*iso*coumarazone*, $C_{11}H_7O_2N_2I$, colourless, silky needles, m. p. 182°; the α-isomeride is not acted on by iodine in glacial acetic acid, but in the presence of iodic acid yields α-4-*iodo*-3-*methylpyrazo*iso*coumarazone*, greenish-yellow needles, m. p. 198°.

3-Methylpyrazo*iso*coumarazone is converted by aqueous-alcoholic ammonia under pressure at 130° into 7-*hydroxy*-3-*methylpyrazoquinazoline*, $C_{11}H_9ON_3$, long, white needles, m. p. 275—276°; the *silver* salt, $C_{11}H_8ON_3Ag$, forms small, white needles; the *chloro*-derivative, $CMe\left\langle\begin{matrix} N{-}N\cdot C_6H_4 \\ CH{:}C{-}NCl \end{matrix}\right\rangle CO$, formed by the action of calcium hypochlorite

on a solution of the quinazoline in aqueous alkali, crystallises in small, red needles, m. p. 275°. 7-Hydroxy-3-methylpyrazoquinazoline is converted (1) by phosphorus oxychloride into *7-chloro-3-methylpyrazoquinazoline*, $C_{11}H_8N_3Cl$, which crystallises in glistening, yellow needles, m. p. 139°, and when treated with an alcoholic solution of sodium ethoxide yields *7-ethoxy-3-methylpyrazoquinazoline*, $C_{13}H_{13}ON_3$, glistening, white, felted needles, m. p. 125°, and (2) by phosphorus pentachloride into *4 : 7-dichloro-3-methylpyrazoquinazoline*, $C_{11}H_7N_3Cl_2$, crystallising in glistening, yellow needles, m. p. 174—175°.

3-Methyl-6-ethyldihydropyrazoquinazolone,

$$CMe\begin{cases}N-N\cdot C_6H_4\\ \quad\;\, | \\ CH{:}C-NEt\end{cases}CO,$$

is prepared by the action of ethylamine on methylpyrazo*iso*coumarazone; it forms glistening, pale yellow needles, m. p. 133—134°; the corresponding *6-phenyl* compound, $C_{17}H_{13}ON_3$, similarly prepared by using aniline, crystallises in colourless needles, m. p. 156°; the corresponding *6-anilino*-compound, $C_{17}H_{14}ON_4$, obtained by using phenylhydrazine, forms lemon-yellow leaflets, m. p. 195°; the corresponding *6-amino*-compound, $CMe\begin{cases}N-N\cdot C_6H_4\\ CH{:}C\cdot N(NH_2)\end{cases}CO$, prepared by heating methylpyrazo*iso*coumarazone with hydrazine hydrate at 180°, crystallises in colourless needles, m. p. 249°, and condenses with benzaldehyde and benzophenone, yielding the *benzylidene* derivative, $C_{11}H_8ON_3\cdot N{:}CHPh$, white needles, m. p. 174°, and *diphenylmethylene* derivative, $C_{11}H_8ON_3\cdot N{:}CPh_2$, white needles, m. p. 257° respectively; the corresponding *carbamide*,

$$C_{11}H_8ON_3\cdot NH\cdot CO\cdot NH_2,$$

prepared by the action of semicarbazide on methylpyrazo*iso*coumarazone, crystallises in needles, m. p. 265°.

4-Bromo-1-phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid,

$$C_{11}H_9O_3N_2Br,$$

is formed by the action of aqueous sodium hydroxide on either of the 4-bromo-3-methylpyrazo*iso*coumarazones; it forms colourless needles, m. p. 202°.

1-Phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid,

$$\begin{matrix}CH_2\cdot CO\\ | \\ CMe{=}N\end{matrix}>N\cdot C_6H_4\cdot CO_2H,$$

similarly prepared from the methylpyrazo*iso*coumarazones, forms slightly yellow crystals, m. p. 195°; the *4-oximino*-derivative,

$$C_{11}H_9O_4N_3,$$

crystallises with $1H_2O$ in rosettes of yellow needles, m. p. 139°; the anhydrous substance has m. p. 200°; the *4-benzylidene* derivative, $C_{18}H_{14}O_3N_2$, forms white crystals, m. p. 243°; the *4-benzeneazo*-derivative, $C_{17}H_{14}O_3N_4$, crystallises in golden-yellow needles, m. p. 205°.

[With JULIUS LEO.]—The following compounds are prepared by methods similar to those employed in the preparation of the corresponding compounds just described: *1-o-tolyl-3 : 4-dimethyl-5-pyrazolone*, $C_{12}H_{14}ON_2$, forms white needles, m. p. 179°; *5-chloro-1-o-tolyl-3 : 4-dimethylpyrazole*, $C_{12}H_{13}N_2Cl$, is a white, crystalline mass, m. p. 48°;

the *methiodide*, $C_{12}H_{13}N_2Cl,MeI$, forms white, silky, felted needles, m. p. 187°; *5-chloro-1-phenyl-3-methylpyrazole-4 : 2'-dicarboxylic acid*, $C_{12}H_9O_4N_2Cl$, crystallises in slender, white needles, m. p 226° (decomp.); the latter substance yields 3-methylpyrazo*iso*coumarazone when distilled under a pressure of 16 mm. at 201°, and *3-methylpyrazo*-iso*coumarazone-4-carboxylic acid*, $C_{12}H_8O_4N_2$, slightly yellow, slender needles, m. p. 224° (decomp.), when heated at 171° under a pressure of 16 mm.; *3-phenyl-1-o-tolyl-5-pyrazolone*, $C_{16}H_{14}ON_2$, crystallises in glistening, white leaflets, m. p. 191°; *5-chloro-3-phenyl-1-o-tolylpyrazole*, $C_{16}H_{13}N_2Cl$, is a white, crystalline mass, m. p. 46°; *5-chloro-1 : 3-diphenylpyrazole-2'-carboxylic acid*, $C_{16}H_{11}O_2N_2Cl$, crystallises with $1H_2O$ in stout, white prisms, m. p. 239° (decomp.); *ethyl benzoylacetate o-carboxyphenylhydrazone*, $CO_2Et\cdot CH_2\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot CO_2H$, forms slender, yellow needles, m. p. 166—167°; *3-phenylpyrazo*iso*coumarazone*, $C_{16}H_{10}O_2N_2$, crystallises in glistening, slender, white needles, m. p. 199°; *4-bromo-3-phenylpyrazo*iso*coumarazone*, $C_{16}H_9O_2N_2Br$, forms glistening, white needles, m. p. 187°; the corresponding *4-chloro*-compound crystallises in slender, white needles, m. p. 170°; *7-hydroxy-3-phenylpyrazoquinazoline*, $C_{16}H_{11}ON_3$, crystallises in felted, white needles, m. p. 315°; the crystalline *potassium* and *silver* salts were analysed; *4 : 6-dichloro-3-phenyldihydropyrazoquinazolone*, $C_{16}H_9ON_3Cl$, forms slender, silky, yellow needles, m. p. 243—248°; *7-chloro-3-phenylpyrazoquinazoline*, $C_{16}H_{10}N_3Cl$, crystallises in glistening, slightly yellow needles, m. p. 145°; *4 : 7-dichloro-3-phenylpyrazoquinazoline*, $C_{16}H_9N_3Cl_2$, forms yellow needles, m. p. 160°; *7-amino-3-phenylpyrazoquinazoline*, $C_{16}H_{12}N_4$, forms white, silky needles, m. p. 215°; *7-ethoxy-3-phenylpyrazoquinazoline*, $C_{18}H_{15}ON_3$, crystallises in glistening, white needles, m. p. 136°; *3-phenyl-6-ethyldihydropyrazoquinazolone*, $C_{18}H_{15}ON_3$, forms glistening, white needles, m. p. 171°; the corresponding *6-phenyl* compound, $C_{22}H_{15}ON_3$, crystallises in pale yellow prisms, m. p. 211°; the corresponding *6-anilino*-compound, $C_{22}H_{16}ON_4$, forms glistening, yellow leaflets, m. p. 248°; the analogous *6-amino*-compound, $C_{16}H_{12}ON_4$, forms glistening, white leaflets, m. p. 232° (decomp.), the *benzylidene* derivative of which crystallises in slender, white needles, m. p. 185°; the *6-carbamide*, $C_{17}H_{13}O_2N_5$, forms felted, white needles, m. p. 325° (decomp.); the *6-oximino*-compound, $C_{16}H_{11}O_2N_3$, forms glistening, white needles, m. p. 247°; *1 : 3-diphenyl-5-pyrazolone-2'-carboxylic acid*, $\begin{matrix} CH_2\cdot CO \\ | \\ CPh{=}N \end{matrix}\!\!>\!N\cdot C_6H_4\cdot CO_2H$, crystallises in white, glistening leaflets, sinters at 189°, m. p. 197° (decomp.), and yields a *barium* salt ($3H_2O$), felted, white needles, *ethyl* ester,

$$C_{16}H_{11}O_2N_2\cdot OEt,$$

glistening, white needles, m. p. 133°, and *dichloro*-derivative,

$$\begin{matrix} CHCl\cdot CCl(OH) \\ | \\ CPh{=\!=\!=\!=\!=\!=}N \end{matrix}\!\!>\!N\cdot C_6H_4\cdot CO_2H,$$

slender, white needles, m. p. 208° (decomp.); *1 : 3-diphenyl-4-benzylidene-5-pyrazolone-2'-carboxylic acid*, $C_{23}H_{16}O_3N_2$, forms glistening, white crystals, m. p. 241°; the corresponding *4-oximino*-compound, $C_{16}H_{11}O_4N_3$, crystallises in stout, scarlet needles, m. p. 213°; the

corresponding 4-*nitro*-compound, $C_{16}H_{11}O_5N_3$, forms glistening, yellow leaflets, m. p. 268° (decomp.); the 4-*benzeneazo*-compound, $C_{22}H_{16}O_3N_4$, forms compact, glistening, bright red crystals, m. p. 225°; the 4-p-*tolueneazo*-compound, $C_{23}H_{18}O_3N_4$, crystallises in glistening, orange-red needles, m. p. 194°.

3-Phenylpyrazo*iso*coumarazone, when heated with phenol and aluminium chloride, yields the *substance*,

$$CPh<\begin{matrix} N—N\cdot C_6H_4 \\ CH\!:\!C——O \end{matrix}>C(C_6H_4\cdot OH)_2,$$

an amorphous, yellowish-brown powder, m. p. 120°, solutions of which in aqueous alkalis are intensely red; an analogous *substance*,

$$C_{32}H_{30}ON_4,$$

is similarly obtained by condensation with dimethylaniline; it forms glistening, white leaflets, m. p. 216°; an intensely green *substance* is formed simultaneously.

3-Methylpyrazo*iso*coumarazone, when heated with resorcinol and zinc chloride, yields a *substance*, $C_{19}H_{14}O_5,2H_2O$, which crystallises in colourless, glistening needles, m. p. 186—187°, and dissolves in alkalis, forming solutions with an intense blue fluorescence; 3-phenyl-pyrazo*iso*coumarazone, when similarly treated, yields a *substance*, $C_{19}H_{12}O_4$, pale yellow, rectangular plates, m. p. 248°, solutions of which in alkali exhibit a yellowish-green fluorescence.

[With CHRISTOPH KÄDING.]—3-*Chloro*-1-*phenyl*-5-*methylpyrazole*-2'-*carboxylic acid*, $C_{11}H_9O_2N_2Cl$, is prepared by the oxidation of 3-chloro-1-*o*-tolyl-5-methylpyrazole with chromic acid; it crystallises with $1H_2O$ in white prisms, m. p. 79°; the anhydrous substance has m. p. 111°; the *barium* and *silver* salts were analysed; the *ethyl* ester,

$$C_{13}H_{13}O_2N_2Cl,$$

is a colourless oil, b. p. 325°. The acid when heated at 190° under a pressure of 16 mm. yields 5-*methylbenzobis*-3-*pyrazolone*,

$$\begin{matrix} C_6H_4\cdot N\cdot CMe \\ CO—N—CO \end{matrix}>CH,$$

crystallising in glistening, yellow leaflets, m. p. 265°, solutions of which in acetic acid, alcohol, and chloroform have a bluish-green or blue fluorescence; the 4-*bromo*-derivative, $C_{11}H_7O_2N_2Br$, forms yellow, matted needles, m. p. 233°, solutions of which in organic solvents exhibit a blue fluorescence. 1-*Phenyl*-5-*methyl*-3-*pyrazolone*-2'-*carboxylic acid*, $C_{11}H_{10}O_3N_2$, is formed by dissolving 5-methylbenzobis-3-pyrazolone in aqueous alkali; it crystallises in white leaflets, m. p. 221°; the *ammonium* salt forms white prisms, m. p. 260°; the *ethyl* ester crystallises in white, slender prisms, m. p. 160°; the *amide*, $C_{11}H_{11}O_2N_3$, is formed by heating 5-methylbenzobis-3-pyrazolone with aqueous ammonia under pressure at 210°; it forms white crystals, m. p. 249°; the *anilide*, $C_{17}H_{15}O_2N_3$, white crystals, m. p. 161°, *phenylhydrazide*, $C_{17}H_{16}O_2N_4$, white leaflets, m. p. 218°, and *hydrazide*, $C_{11}H_{12}O_2N_4$, colourless crystals, m. p. 253°, are similarly prepared; the 4-*benzeneazo*-derivative, $C_{17}H_{14}O_3N_4$, forms yellowish-brown leaflets, m. p. 210°.

4-*Bromo*-1-o-*tolyl*-3-*methylpyrazole*, $C_{11}H_{11}N_2Br$, is prepared by brominating 1-*o*-tolyl-3-methylpyrazole; it is a colourless liquid with

a pleasant odour, b. p. 171°/25 mm., and when oxidised yields 4-*bromo-1-phenyl-3-methylpyrazole-2′-carboxylic acid*, $C_{11}H_9O_2N_2Br$, which crystallises in white prisms, m. p. 194°; the *silver* salt forms white needles; the *ethyl* ester is a colourless oil with a pleasant odour, b. p. 334°. W. H. G.

1-Phenyl-3-methyl 5-pyrazolone-3′- and 4′-carboxylic Acids. AUGUST MICHAELIS and HANS HORN (*Annalen*, 1910, **373**, 213—218).—The 3′- and 4′-carboxylic acids of 1-phenyl-3-methyl-5-pyrazolone have the same chemical properties as the 2′-isomeride (compare this vol., i, 514), but the chloropyrazolecarboxylic acids derived from them, when heated, do not decompose with the elimination of hydrogen chloride.

Ethyl acetoacetate-4-carboxyphenylhydrazone,

$$CO_2Et\cdot CH_2\cdot CMe\colon N\cdot NH\cdot C_6H_4\cdot CO_2H,$$

is prepared from ethyl acetoacetate and 4-hydrazinobenzoic acid; it forms slightly yellow needles, and when heated at 150° yields 1-*phenyl-3-methyl 5 pyrazolone-4′-carboxylic acid*, $C_{11}H_{10}O_3N_2$, pale yellow needles, m. p. 281°; the latter substance is converted (1) by benzaldehyde into the 4-*benzylidene* derivative,

$$C_{10}H_8O_3N_2\cdot C\colon CHPh,$$

dark red needles, m. p. 266°; (2) by sodium nitrite and acetic acid into the 4-*oximino*-derivative, $C_{10}H_8O_3N_2\cdot C\colon N\cdot OH$, yellow needles, decomposing at 253°; (3) by diazobenzene chloride into the 4-*benzeneazo*-derivative, $C_{10}H_8O_3N_2\cdot C\colon N_2Ph$, slender, yellow needles, m. p. 277°, and (4) by phosphoryl chloride into 5-chloro-1-phenyl-3-methylpyrazole 4′-carboxylic acid (compare Michaelis and Sudendorf, Abstr., 1900, i, 696).

The following compounds are similarly prepared: 1-*phenyl-3-methyl-5-pyrazolone-3′-carboxylic acid* forms slender, white needles, m. p. 217°; the *methyl* ester forms white crystals, m. p. 86°; the *ethyl* ester is a pale yellow oil, b. p. 241°/25 mm.; the 4-*benzylidene* derivative crystallises in red leaflets, m. p. 251°; the 4-*oximino*-derivative forms orange-red needles, m. p. 242°; the 4-*benzeneazo*-derivative forms orange-yellow leaflets, m. p. 245°; 5-*chloro-1-phenyl-3-methylpyrazole-3′-carboxylic acid* crystallises in small needles, m. p. 165°. 1-Phenyl-3-methyl-5-pyrazolone-3′-carboxylic acid (1 mol.) is converted by phosphorus pentachloride (2 mols.) under pressure at 136°, and subsequent treatment with water into 4 : 4-*dichloro-1-phenyl-3-methyl-5-pyrazolone-3′-carboxylic acid*,

$$C_{11}H_8O_3N_2Cl_2,$$

white needles, m. p. 116°. W. H. G.

Blue Reduction Product from Flavanthren. JULIUS POTSCHIWAUSCHEG (*Ber.*, 1910, **43**, 1748—1750).—Flavanthren, when reduced with alkaline sodium hyposulphite in an atmosphere of hydrogen, yields a mixture of products from which Scholl and Holdermann (Abstr., 1908, i, 696) by means of benzoyl chloride isolated *O*-benzoyldihydroflavanthren, an amorphous, reddish-brown powder.

Using *p*-bromobenzoyl chloride, a *mono-p-bromobenzoyldihydroflavanthren* is obtained, crystallising from nitrobenzene in yellow needles, which are not melted at 360°. This is insoluble in sodium

hydroxide; accordingly, the acyl residue is attached to oxygen. It dissolves in concentrated sulphuric acid with a green coloration, turning reddish-brown on heating. E. F. A.

Intramolecular Transformations. IV. Hydroxytriazoles and Diazoamides. OTTO DIMROTH [and, in part, HANS AICKELIN, B. BRAHN, GUSTAV FESTER, and ELSA MERCKLE] (*Annalen*, 1910, **373**, 336—370. Compare Abstr., 1905, i, 98, 384; 1909, i, 267).—It has been shown previously that many 5-hydroxy-1 : 2 : 3-triazole derivatives are converted by fusion or by solution in organic solvents into neutral isomerides which have been regarded as triazolones, the change being one of enol-keto-desmotropy. Doubts of the correctness arose later when it was found that 5-aminotriazoles under the same conditions also underwent changes by detachment of the azo-group from one nitrogen atom and re-attachment to another; for example:

$$\mathrm{NR}<{\mathrm{C(NHR')}\atop \mathrm{N{=}{=}N}}>\mathrm{CH} \longrightarrow \mathrm{NR'}<{\mathrm{C(NHR)}\atop \mathrm{N{=}{=}N}}>\mathrm{CH}.$$

Assuming that the same change occurs in hydroxytriazoles, the neutral isomeride would be a substituted amino-derivative of a diazo-anhydride: $\mathrm{NR}<{\mathrm{C(OH)}\atop \mathrm{N{=}N}}>\mathrm{CH} \longrightarrow \mathrm{O}<{\mathrm{C(NHR)}\atop \mathrm{N{=}{=}N}}>\mathrm{CH}$. This explanation of the change of the hydroxytriazoles has been considered previously and rejected, because the properties of the neutral isomerides are not at all comparable with those of other diazo-anhydrides, the cyclic oxygen atom of which is very reactive (Wolff, Abstr., 1903, i, 203). Piloty and Neresheimer (Abstr., 1906, i, 146) have shown, however, that ethyl diazomalonate exhibits remarkable stability to acids and to iodine, and therefore formulate it as a diazo-anhydride, ${\mathrm{C(CO_2Et)\colon C(OEt)}\atop \mathrm{N{=}{=}{=}{=}N}}>\mathrm{O}$. The oxygen atom is non-reactive, showing no tendency to be replaced by sulphur or amino-groups. The stability of ethyl diazomalonate is not remarkable when it is borne in mind how the reactivity of diazomethane is diminished by the introduction of one carbethoxy-group. Consequently, ethyl diazomalonate may be represented by the preceding formula or by the only alternative, ${\mathrm{N}\atop \mathrm{N}}>\mathrm{C(CO_2Et)_2}$. The latter is accepted for the following reasons: Ethyl diazomalonate is converted by cold ammonium hydroxide into ethyl diazomalonamate, $\mathrm{NH_2 \cdot CO \cdot CN_2 \cdot CO_2Et}$, m. p. 143°, which is changed by sodium ethoxide into *ethyl* 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*carboxylate*, ${\mathrm{C(CO_2Et)\colon C(OH)}\atop \mathrm{N{=}{=}{=}{=}N}}>\mathrm{NH}$, m. p. 130°; the latter is reconverted into the former by fusion. If ethyl diazomalonate has the constitution ascribed to it by Piloty and Neresheimer, the substance produced by the action of ammonium hydroxide would be either ${\mathrm{C(CO_2Et)\colon C(NH_2)}\atop \mathrm{N{=}{=}{=}{=}N}}>\mathrm{O}$ or ${\mathrm{C(CO \cdot NH_2)\colon C(OEt)}\atop \mathrm{N{=}{=}{=}{=}N}}>\mathrm{O}$, neither of which is satisfactory, since the substance does not contain a primary amino-group, and yields a hydroxytriazolecarboxylic ester (not an amide) by treatment with sodium ethoxide.

From the preceding, the author arrives at the conclusion that all the

neutral isomerides, obtained by the fusion or solution of 5-hydroxytriazoles and previously described as triazolones, possess a diazo-structure similar to that of ethyl diazomalonate, and are derivatives of diazomethane. This theory harmonises with the fact that the hydroxytriazoles are colourless, whilst their neutral isomerides are yellow, and explains such phenomena as the conversion of 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid into carbon dioxide and the corresponding hydroxytriazole by warm water, and the conversion of the neutral isomeride

$$\left[\text{new formula, } NHPh\cdot CO\cdot C(CO_2H)<\overset{N}{\underset{N}{\|}}\right]$$

by the same means into nitrogen and glycolloanilide. The theory is supported by the two following facts. Aminomalonamide hydrochloride in aqueous solution, sodium nitrite, and a few drops of dilute sulphuric acid at 0° yields *diazomalonamide*, $\overset{N}{\underset{N}{\|}}>C(CO\cdot NH_2)_2$, m. p. 175°, which forms yellow crystals, and is converted by sodium ethoxide into 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*carboxylamide*,

$$\begin{matrix} C(CO\cdot NH_2)\colon C(OH) \\ | \qquad\qquad\qquad \\ N=\!=\!=\!=\!=\!=\!=\!=N \end{matrix}>NH,$$

m. p. 196°, which is colourless and reconvertible into diazomalonamide by prolonged boiling with alcohol. (The hydroxytriazole-amide is more conveniently prepared by acidifying the product obtained by the interaction of malonamide, phenylazoimide, and alcoholic sodium ethoxide.) The other fact is the reduction of the substance formerly described as methyl 1-phenyl-5-triazolone-4-carboxylate

$$\left[\text{now regarded as } NHPh\cdot CO\cdot C(CO_2Me)<\overset{N}{\underset{N}{\|}}\right]$$

by alcoholic hydrogen sulphide to a *hydrazi*-compound,

$$NHPh\cdot CO\cdot C(CO_2Me)<\overset{NH}{\underset{NH}{|}},$$

m. p. 130—131°, which is colourless, does not decolorise iodine, yields hydrazine by treatment with boiling 10% hydrochloric acid, and is reconverted into the original substance by mercuric oxide; this behaviour is quite similar to that of the reduction product of ethyl diazomalonate.

The analogy between the desmotropic change of 5-hydroxytriazoles and of 5-aminotriazoles, which apparently disappears in the new explanation of the former change, reappears with the assumption of the formation of a fugitive intermediate compound in the case of the aminotriazoles; thus, $\begin{matrix} C(CO_2R)\colon C(NH_2) \\ | \qquad\qquad \\ N=\!=\!=\!=\!=\!=N \end{matrix}>NPh \longrightarrow$

$$NPh\colon C(NH_2)\cdot C(CO_2R)<\overset{N}{\underset{N}{\|}} \longrightarrow \begin{matrix} C(CO_2R)\colon C(NHPh) \\ | \qquad\qquad \\ N=\!=\!=\!=\!=\!=\!=N \end{matrix}>NH.$$

It appears, therefore, that there is an intimate connexion between hydroxytriazoles of the type $\begin{matrix} CR'\colon C(OH) \\ | \qquad \\ N=\!=\!=\!=N \end{matrix}>NR$ and diazoamides, $NHR\cdot CO\cdot CR'<\overset{N}{\underset{N}{\|}}$. The latter are converted quantitatively and universally into salts of the former by alkaline reagents. The

converse change, hydroxytriazole $\longrightarrow$ diazoamide, by fusion or solution in organic solvents is not general, and depends on the nature of R and R. 5-Hydroxytriazole, 5-hydroxy-1-phenyltriazole, 5-hydroxy-1-phenyl-4-methyltriazole, and 5-hydroxy-1 : 4-diphenyltriazole cannot be changed into the isomeric diazoamides. The presence of CO_2R or of $CO{\cdot}NH_2$ in position 4 facilitates the change into the diazo-compound, which is also favoured by the presence of phenyl and especially of negatively-substituted phenyl groups in position 1; thus methyl 5-hydroxy-1-*o*-*p*-dinitrophenyl-1 : 2 : 3-triazole-4-carboxylate has so great a tendency to change that it is only stable in the form of its salts. Also, when *p*-nitrophenylazoimide and methyl sodiomalonate react in methyl alcohol, and the product is acidified and recrystallised from acetic acid, the yellow *diazo*-compound,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C(CO_2Me){<}\genfrac{}{}{0pt}{}{N}{\overset{||}{N}},$$

m. p. 175°, is obtained, the expected colourless hydroxytriazole, $\genfrac{}{}{0pt}{}{C(CO_2Me){:}C(OH)}{N=\!=\!=\!=\!=\!=N}{>}N{\cdot}C_6H_4{\cdot}NO_2$, only being produced by treating the yellow isomeride with sodium methoxide.

The stabilising influence of a positive radicle in position 1 is shown in the case of *methyl* 5-*hydroxy*-1-*benzyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, m. p. 119°, which is obtained from benzylazoimide, methyl malonate, and methyl alcoholic sodium methoxide, and subsequent acidification of the product; it is colourless, and can be recrystallised from organic solvents without change, although by fusion it is converted into the yellow *diazo*-compound, $CH_2Ph{\cdot}NH{\cdot}CO{\cdot}C(CO_2Me){<}\genfrac{}{}{0pt}{}{N}{\overset{||}{N}}$, m. p. 45°.

Methods of measuring the velocities of the opposed reactions, hydroxytriazole $\rightleftarrows$ diazo-compound, are described, and the values are tabulated and discussed. C. S.

Urazoles. XVI. Salts of Tautomeric Compounds. Reactions of Urazole Salts with Alkyl Halides. ROGER F. BRUNEL and SALOMON F. ACREE (*Amer. Chem. J.*, 1910, **43**, 505—553. Compare Abstr., 1908, i, 919).—An account is given of a study of the alkylation of potassium phenylurazole by various alkyl iodides. The chief product of these reactions is the *N*-ester of the urazole, and, in most cases, evidence was obtained of the presence of some *O*-ester. In the case of the *iso*butyl and *iso*amyl compounds, only traces of *O*-derivatives could be detected, whilst in other cases the amount appeared to be 10—20% of the total product.

The application of the results of these experiments to the general question of tautomerism is discussed. It is shown that the assumption of different structures for the potassium and silver salts of a tautomeric compound does not afford an explanation of the urazole reactions, since both salts yield a mixture of *O*- and *N*-esters. The theory that when a salt gives two isomeric derivatives on alkylation, one is an intermediate product in the formation of the other, does not hold in the present case, because neither derivative undergoes rearrangement into the other, and the ratio of the two products is almost the same at all

stages of the reaction. The addition theory is not valid in the case of the urazoles, since in many reactions the velocity decreases on the addition of electrolytes, whereas, according to this theory, it should increase. The results can all be explained, however, by assuming the existence of two tautomeric salts in instantaneous equilibrium.

The following compounds have been obtained: 1-*phenyl*-2-*ethylurazole*, m. p. 119°; 1-*phenyl*-2-n-*propylurazole*, m. p. 128°; 1-*phenyl*-2-n-*butylurazole*, m. p. 130°; 1-*phenyl*-2-iso*propylurazole*, m. p. 161·5°; 1-*phenyl*-2-iso*butylurazole*, m. p. 152·5°; 1-*phenyl*-2-iso*amylurazole*, m. p. m. p. 97—98°. The *silver* salts of all these compounds, except the last, have been prepared. 1-*Phenyl*-4-n-*propylurazole* has m. p. 120°; 1-*phenyl*-4-n-*butylurazole*, m. p. 149—150°, and 1-*phenyl*-4-*methyl*-2-*ethylurazole*, m. p. 52—53°.

In carrying out the quantitative investigation of the reaction of the alkyl halides with urazole salts, it was necessary to maintain sealed tubes at a particular temperature for a considerable time. For this purpose a special constant-temperature water-bath was devised, which is regulated automatically and can be kept at any temperature up to 100° with a variation of not more than 0·1—0·2°. This apparatus is described. E. G.

Degradation of 7 : 9-Dimethyluric Acid. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, 43, 1589—1600).—When 7 : 9-dimethyluric acid 4 : 5-diglycol (Fischer's oxy-7 : 9-dimethyluric acid : compare this vol., i, 526) is heated with water or with glacial acetic acid on the water-bath for several hours, it is transformed into an isomeride, which is represented as 5-*hydroxy*-1 : 3-*dimethylhydantoin*-5-*carbureide* or 5-*hydroxy*-1 : 3-*dimethylhydantoylcarbamide*,

$$\mathrm{NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C(OH)}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{CO{-}{-}NMe}\end{matrix},$$

which crystallises from a mixture of ether and alcohol. It has m. p. 208° (decomp.), and when decomposed with sodium hydroxide solution at the ordinary temperature is transformed into the corresponding acid, which immediately loses water, yielding the lactone,

$$\begin{matrix}\overset{7}{\mathrm{N}}\mathrm{H{\cdot}}\overset{6}{\mathrm{C}}\mathrm{O}\\ \underset{8}{\mathrm{C}}\mathrm{O{-}{-}O}\end{matrix}>\underset{5}{\mathrm{C}}<\begin{matrix}\overset{1}{\mathrm{N}}\mathrm{Me{\cdot}}\overset{2}{\mathrm{C}}\mathrm{O}\\ \underset{4}{\mathrm{C}}\mathrm{O{-}{-}}\underset{3}{\mathrm{N}}\mathrm{Me}\end{matrix},$$

which is closely related to certain degradation products of caffeine, and is therefore termed 1 : 3-*dimethylcaffolide*. It crystallises from chloroform in flat, monoclinic rhombohedra, m. p. 163—164° (decomp.). A quantitative yield of the same compound can be obtained by treating an alcoholic solution of hydroxydimethylhydantoylcarbamide with hydrogen chloride.

When boiled with water, the dimethylcaffolide takes up a molecule of water and loses carbon dioxide, yielding 1 : 3-*dimethylhydantoylamide*, $\mathrm{NH_2{\cdot}CO{\cdot}C(OH)}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{CO{-}{-}NMe}\end{matrix}$, which crystallises in large, mono- or tri-clinic prisms, m. p. 180—182° (decomp.). The *ethyl ether*,

$$\mathrm{NH_2{\cdot}CO{\cdot}C(OEt)}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{CO{-}{-}NMe}\end{matrix},$$

obtained by saturating the alcoholic solution with hydrogen chloride, crystallises in six-sided prisms, m. p. 189—190°, and the *diacetyl* derivative, $C_{10}H_{13}O_6N_3$, crystallises in flat, rectangular prisms, m. p. 172—173°.

Cholesterophan is formed when 5-hydroxy-1 : 3-dimethylhydantoylamide is oxidised with nitrous acid or with dichromate and sulphuric acid, and also when the amide is distilled. Mesoxalic acid and dimethylcarbamide are formed when the amide is boiled with barium hydroxide solution. Hydrogen peroxide and ammonia react with the amide, yielding cholesterophan and formic acid. When heated at 210°, the amide loses carbon dioxide and yields a product, m. p. 330° (decomp.), which is regarded as *5-hydroxy-1 : 3-dimethylhydantoin-5-carboxylic acid lactamide*,

$$\begin{array}{l}\text{NMe–CO}\\ \text{CO·NMe}\end{array}\!\!>\!C\!<\!\!\begin{array}{l}\text{NH·CO}\\ \text{CO·NH}\end{array}\!\!>\!C\!<\!\!\begin{array}{l}\text{NMe·CO}\\ \text{CO—NMe}\end{array}.$$

J. J. S.

Degradation of Tetramethyluric Acid. *allo*Caffeine. HEINRICH BILTZ (*Ber.*, 1910, 43, 1600—1618. Compare Schmidt and Schilling, Abstr., 1885, 995; Fischer, Abstr., 1898, i, 180; Torrey, Abstr., 1899, i, 86).—The constitution of *allo*caffeine has been established by its synthesis from 1:3-dimethylcaffolide (compare preceding abstract) by the methylation of the *silver* salt, $C_7H_6O_5N_3Ag$, and by means of methyl iodide and silver oxide. *allo*Caffeine is therefore *1 : 3 : 7-trimethylcaffolide*, $\begin{array}{l}\text{NMe·CO}\\ \text{CO——O}\end{array}\!\!>\!C\!<\!\!\begin{array}{l}\text{NMe·CO}\\ \text{CO—NMe}\end{array}$.

The degradation of tetramethyluric acid to *allo*caffeine probably proceeds in the following stages: (1) Oxidation to the corresponding glycol; (2) rupture of the alloxan ring at position 3 : 4, and formation of 5-hydroxy-1 : 3-dimethylhydantoyl-7 : 9-dimethylcarbamide; (3) hydrolysis to methylamine and the hydroxy acid; (4) elimination of water and formation of the lactone.

Attempts have been made to prepare tetramethyluric acid glycol by the condensation of dimethylalloxan with dimethylcarbamide, but the reaction proceeds further, and methylamine and *allo*caffeine are the only products obtained. This method is the most convenient for the preparation of *allo*caffeine, especially when the condensation is carried out in the presence of dilute hydrochloric acid (1 : 2) at the ordinary temperature, as under these conditions a 95% yield of *allo*caffeine is obtained at the end of two days. *allo*Caffeine can also be obtained by the condensation of methylalloxan with dimethylcarbamide, and by the methylation of 5-hydroxy-1 : 3-dimethylhydantoylcarbamide (preceding abstract) with methyl sulphate.

*allo*Caffuric acid, obtained by boiling an aqueous solution of *allo*caffeine (Torrey, *loc. cit.*), has m. p. 168·5—169·5° after it has been once fused. This method of formation is analogous to the conversion of 1:3-dimethylcaffolide into 5-hydroxy-1:3-dimethylhydantoylamide (preceding abstract). *allo*Caffuric acid is therefore *5-hydroxy-1 : 3-dimethylhydantoylmethylamide*, $\text{NHMe·CO·C(OH)}\!<\!\!\begin{array}{l}\text{NMe·CO}\\ \text{CO—NMe}\end{array}$, and its reactions are in complete harmony with this constitution. When

distilled, it yields cholesterophan and methylformamide, and when hydrolysed with barium hydroxide yields methylamine, mesoxalic acid, and dimethylcarbamide.

5-*Acetyl*allo*caffuric acid*, $C_9H_{13}O_5N_3$, crystallises in well-developed twinned prisms, m. p. 194·5—195·5°. The *ethyl ether*, 5-*ethoxy*-1 : 3-*dimethylhydantoylmethylamide*, $NHMe\cdot CO\cdot C(OEt)<\begin{matrix}NMe\cdot CO\\ |\\ CO\text{—}NMe\end{matrix}$, obtained by saturating an alcoholic solution of the hydroxy-compound with hydrogen chloride at 0°, crystallises in well-developed, monoclinic prisms, m. p. 112—113°. The corresponding *methyl ether*, $C_8H_{13}O_4N_3$, has m. p. 121—122°.

1 : 3-*Dimethylhydantoylmethylamide* (*deoxy*allo*caffuric acid*),

$$NHMe\cdot CO\cdot CH<\begin{matrix}NMe\cdot CO\\ |\\ CO\text{—}NMe\end{matrix},$$

obtained by reducing *allo*caffuric acid with hydriodic acid (D = 1·96), crystallises from alcohol in flat prisms, m. p. 180°, after sintering at 170°, and can be oxidised by chlorine water to *allo*caffuric acid.

*allo*Caffeine reacts with a cold 33% alcoholic methylamine solution, yielding *allo*caffuric acid and dimethylcarbamide. The reaction probably consists in the addition of methylamine to the *allo*caffeine, yielding 5-hydroxytetramethylhydantoylcarbamide, which at once reacts with methylamine, forming *allo*caffuric acid and dimethylcarbamide. Ethylamine and ammonia react in a similar manner.

Schmidt and Schilling's caffeinemethylhydroxide (*loc. cit.*) is to be represented by the formula : $CO<\begin{matrix}NMe\cdot CO\cdot C\cdot NMe\text{———}\\ \| \\ NMe\text{———}C\cdot NMe(OH)\end{matrix}>CH.$

J. J. S.

*apo*Caffeine and the Degradation of 1 :3 : 7-Trimethyluric Acid and of Caffeine. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, 43, 1618—1632. Compare Fischer, Abstr., 1882, 217, 628 ; 1897, i, 267—268).—*apo*Caffeine is 1 : 7-*dimethylcaffolide*,

$$\begin{matrix}NMe\cdot CO\\ |\\ CO\text{——}O\end{matrix}>C<\begin{matrix}NMe\cdot CO\\ |\\ CO\text{——}NH\end{matrix},$$

as its *silver* salt, $C_7H_6O_5N_3Ag$, yields *allo*caffeine when treated with silver oxide and methyl iodide. Similarly, caffuric acid is 5-hydroxy-1-methylhydantoylmethylamide, as it yields *allo*caffuric acid when methylated.

The best method of obtaining *apo*caffeine is the oxidation of caffeine with potassium chlorate and concentrated hydrochloric acid (compare Maly and Andreasch, Abstr., 1882, 629). When dilute hydrochloric acid is used, and excess of acid is avoided, an isomeride, *isoapo*caffeine, is also formed ; the proportions are *apo*caffeine four-fifths, and the *iso*-compound one-fifth. The same *iso*-compound is also formed by the action of potassium chlorate and hydrochloric acid on trimethyluric acid or on chlorocaffeine. It crystallises in four-sided pyramids or in lancet-shaped plates, decomposes at 176—177°, and when methylated yields *allo*caffeine. *apo*Caffeine and *isoapo*caffeine can be synthesised from methylcarbamide and dimethylalloxan in hydrochloric acid solution, and this appears to be the most convenient

method for the preparation of *apo*caffeine; a trimethyluric acid glycol could not be isolated.

The *ethyl ether* of caffuric acid, 5-*ethoxy*-1-*methylhydantoylmethylamide*, $NHMe{\cdot}CO{\cdot}C(OEt){<}\begin{matrix}NMe{\cdot}CO \\ CO{-}{-}NH\end{matrix}$, crystallises in compact prisms, m. p. 220—221°. J. J. S.

Carbon-Nitrogen Linkings. HEINRICH BILTZ (*Ber.*, 1910, 43, 1632—1636).—It is pointed out that the affinities existing between nitrogen and carbon are analogous to the affinities which take part in salt formation.

The compounds formed increase in stability as the basic nature of the nitrogen and the acidic nature of the carbon are increased and vice versa. This accounts for the stability of the glycols formed from 7 and 9 alkylated uric acids. Such compounds when decomposed suffer rupture in the alloxan ring.

Noticeable is the fact that the introduction of methyl groups into the alloxan ring facilitates decomposition to such an extent that it has not been found possible to isolate the glycols of tri- and tetramethyluric acids.

Similar relationships are met with in the glycols derived from diphenylglyoxalones. Various other examples are cited. J. J. S.

Dihydrazines. III. JULIUS VON BRAUN (*Ber.*, 1910, 43, 1495—1505. Compare Abstr., 1908, i, 700, 737).—4 : 4′-Bismethylhydrazinodiphenylmethane (diphenylmethanedimethyldihydrazine) reacts readily with diketones at the ordinary temperature, but only one carbonyl group takes part in the reaction.

Acetonylacetone and 2 : 9-undecandione (Abstr., 1907, i, 893) yield thick, oily condensation products. Acetylacetone yields a *product*, $CH_2(C_6H_4{\cdot}NMe{\cdot}N{:}CMe{\cdot}CH_2Ac)_2$, m. p. 144°, and benzoylacetone, a *product*, $CH_2(C_6H_4{\cdot}NMe{\cdot}N{:}CPh{\cdot}CH_2Ac)_2$, which crystallises in yellow plates, m. p. 147°. Diacetyl yields a product which melts at about 100°.

Contrary to Kohlrausch's statement (Abstr., 1890, 24), it is found that *as*-phenylmethylhydrazine also reacts readily with diketones in acetic acid solution. *Acetylacetonephenylmethylhydrazone*,

$$CH_2Ac{\cdot}CMe{:}N{\cdot}NMePh,$$

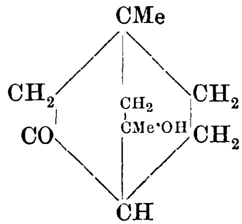
forms long, prismatic crystals, m. p. 98°, and b. p. 165°/12 mm.; the benzoylacetonephenylmethylhydrazone has m. p. 80°, not 103—104°.

Cyclic ketones containing the group $-CH_2{\cdot}CO{\cdot}CH_2-$, and in addition several side-chains, react with the dihydrazine and a little sulphuric acid in the same manner as the ketones described previously (Abstr., 1908, i, 737), but not quite so readily; in each case ammonia is evolved, and an amorphous carbazole condensation product sparingly soluble in alcohol is obtained.

Ethyl 1-methyl*cyclo*hexan-5-one-2-carboxylate yields a product, which on hydrolysis gives an *acid* decomposing at about 200°. The *acid*, obtained by hydrolysing the condensation product from ethyl 1 . 3-dimethyl*cyclo*hexan-5-one 2-carboxylate, has m. p. 171°. Dihydro*iso*phorone yields a *product*, which sinters at 167° and melts at 180°;

ethyl dihydro*iso*phoronecarboxylate, a *product*, m. p. 102°; and ethyl 1-phenyl*cyclo*hexan-3-one-5-acetate, a *product*, which melts at 175° after sintering at 155°.

Carvone, thujone, diosphenol, and dimethyldi*cyclo*nonanolone (Rabe, Abstr., 1908, i, 554) do not react with the dihydrazine. The non-reactivity of the last-mentioned compound indicates that its constitution is probably that of a di*cyclo*octane derivative (annexed formula).



Arabinose, rhamnose, galactose, and mannose react readily with the dihydrazine. Ketoses, dextrose, xylose, glucosamine, lactose, maltose, raffinose, and sucrose do not react. This difference is undoubtedly due to spatial relationships of the hydroxyl groups. The hydrazones formed from arabinose, rhamnose, galactose, and *d*-mannose are obtained in theoretical amount, and can be readily isolated from aqueous alcoholic or dilute acetic acid solutions, as they are sparingly soluble. The products melt respectively at 180° (decomp.), 163°, 185°, 179°. Mixtures of mannose and dextrose and of arabinose and xylose can be separated easily by means of the different behaviour of the sugars towards the dihydrazine.

Diphenylmethanediethyldihydrazine, $CH_2(C_6H_4\cdot NEt\cdot NH_2)_2$, is an oil; it yields a sparingly soluble *sulphate* and a *semicarbazide*,

$$CH_2(C_6H_4\cdot NEt\cdot NH\cdot CO\cdot NH_2)_2,$$

obtained by the action of potassium cyanate, m. p. 215°.

The diethyldihydrazine yields hydrazones with aromatic aldehydes, which can be obtained in a crystalline form from pyridine. Benzaldehyde yields a *product*, $CH_2(C_6H_4\cdot NEt\cdot N:CHPh)_2$, in the form of colourless, glistening plates, m. p. 161°; anisaldehyde, a *product*, $CH_2(C_6H_4\cdot NEt\cdot N:CH\cdot C_6H_4\cdot OMe)_2$, m. p. 142°; glyoxal yields a solid *hydrazone*, $CH_2<\begin{matrix}C_6H_4\cdot NEt\cdot N:CH\\ C_6H_4\cdot NEt\cdot N:CH\end{matrix}$, but most aliphatic aldehydes yield oily hydrazones. The sugars react somewhat more slowly with the diethyl compound. Mannose yields a *hydrazone*,

$$CH_2(C_6H_4\cdot NEt\cdot N:C_6H_{12}O_5)_2,$$

m. p. 183°. J. J. S.

Behaviour of Certain Ureides and Purine Substances towards Sodium Benzoate Solutions. GIOVANNI PELLINI and MARIO AMADORI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 480—487).—The authors have measured the variations produced in the freezing points of water and of solutions of sodium benzoate of a number of different, fixed concentrations by the addition of increasing quantities of certain ureides and purine derivatives (compare this vol., i, 416). The results show that carbamide and urethane behave normally in water and in sodium benzoate solutions. Diethylbarbituric acid ("veronal") gives normal depressions of the freezing point of water, and even with concentrated solutions of sodium benzoate there is neither an appreciable increase of solubility nor sufficient variation of the freezing point to indicate the formation of a compound between the veronal and sodium benzoate. Alloxan behaves normally in water, but forms a

compound with sodium benzoate; allantoin exhibits similar behaviour. The slight solubility of uric acid in water does not appear to be increased in presence of sodium benzoate, whilst the solubility of theobromine is apparently augmented to some extent. Theophylline increases in solubility in presence of sodium benzoate.

No clear relation exists between the dissociation constants of these different compounds and their tendencies to form complexes with sodium benzoate, although caffeine has the smallest dissociation constant and the greatest capacity for complex formation.

T. H. P.

Uric Acid Glycols. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, **43**, 1511—1519).—A comparison of the formulæ of 7 : 9-dimethyluric acid and 1 : 3-dimethyl-4 : 5-diphenylglyoxalone and their oxidation (Abstr., 1908, i, 218) points to the conclusion that Fischer's oxy-7 : 9-dimethyluric acid (Abstr., 1884, 1309) is the glycol:

$$CO<\begin{matrix} NH\cdot CO\cdot C(OH)\cdot NMe \\ NH\text{——}C(OH)\cdot NMe \end{matrix}>CO.$$

This view is shown to be correct, as Fischer's compound can be synthesised by heating together alloxan and dimethylcarbamide, either alone or in acetic acid or concentrated aqueous solution. These methods are much more convenient that Fischer's for the preparation of the glycol. When its solution in glacial acetic acid is heated for a long time, an isomeride is formed. The crystals of the glycol are triclinic, and show cleavage along the base; the angle $b : a = 96°$, $c : a = 98°$, and $a : b = 99°$.

Methylcarbamide and alloxan yield a *methyluric acid glycol*, $C_6H_8O_5N_4$, which crystallises in flat prisms or plates, m. p. 208—209° (decomp.), and it is not so soluble as the dimethyl derivative.

7 : 9-*Diethyluric acid glycol*, $C_9H_{14}O_5N_4$, crystallises in monoclinic prisms, begins to melt at 105°, and becomes quite clear at 120°.

Ethyluric acid glycol, $C_7H_{10}O_5N_4$, crystallises in glistening plates, which decompose at 198—200°.

J. J. S.

Hexanitrohydrazobenzene and Salts of Trinitrodiphenylamine. ARTHUR HANTZSCH and JOSEPH LISTER (*Ber.*, 1910, **43**, 1685—1688).—When a solution of hexanitrohydrazobenzene in methyl alcohol or acetonitrile is evaporated in a desiccator, a residue is obtained of the yellow, real hexanitrohydrazobenzene, together with a red mass which probably consists of a compound of the *aci*-nitro-form and the solvent, since by warming or by treatment with acids the red mass loses weight and changes into yellow hexanitrohydrazobenzene. This view is supported by spectrometric evidence. Yellow solutions of hexanitrohydrazobenzene show only general absorption, whilst red solutions yield absorption spectra very similar to those of the alkali salts of the hexanitro-compound.

C. S.

The Refractive Indices of Solutions of Certain Proteins. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, **7**, 359—364).—If n is the refractive index of the solution, n_1 of the solvent (distilled water, 1·3333 at 18°), c the percentage concentration of the protein, and a a constant equal to the change in the refractive index produced by

dissolving 1 gram in 100 c.c., then $n - n_1 = ac$. The values of a for ovomucoid, ovo-vitellin, and caseinogen respectively are 0·00160, 0·00130, and 0·00152. W. D. H.

Adsorption Compounds of Certain Proteins with Inorganic Haloid Salts Soluble in Alcohol. FRIEDRICH SIMON (*Zeitsch. physiol. Chem.*, 1910, 66, 70—87).—Certain haloid salts (calcium chloride, bromide and iodide, strontium chloride, and lithium chloride) which are soluble in alcohol, when mixed with proteins and protein digestion products in aqueous solutions are precipitated with the proteins in definite quantities on the addition of alcohol. The removal of the salts by washing or by re-solution and precipitation is very difficult and never complete. The precipitates form brown powders on drying, which dissolve easily in warm water; the solutions exhibit the typical reactions of the anions and cations of the salts used; these are present in the same proportions as in the salts. W. D. H.

Calorimetric Investigations of the Precipitation of Proteins by Salts of Heavy Metals. TULLIO GAYDA (*Biochem. Zeitsch.*, 1910, 25, 341—358).—The author determined the heat of reaction when salts of heavy metals in varying strengths of solution are added to protein solutions, and by analysis, the composition of the precipitate formed. If a precipitate is formed in the case of copper salts, there is a fall of temperature. This is the algebraical sum of the heat of solution and the heat of precipitation, which latter factor is negative. This latter is itself the algebraical sum of the heat of precipitation of protein (0·4025 cal. for 1 gram protein, which number is independent of the protein concentration in solution) and the heat of adsorption of copper sulphate by the protein (–20·1621 cal. for 1 gram of copper sulphate). In greater concentrations, when no precipitate is formed, the heat of reaction is the algebraical sum of the heat of dilution of the copper sulphate solution and a residual heat which is negative, and which indicates that even when no precipitate is formed, a complex of protein and copper sulphate is formed. When a precipitate is formed by mercuric salts, the heat of reaction is positive. The conditions here are somewhat more complex than in the case of copper salts, as the heat of adsorption of mercury salts by the protein complex is a function of two variables; namely, the quantity of protein precipitated and the mercury salt carried down with this precipitate. The heat of adsorption of 1 gram of mercuric chloride is a parabolic function of the quantity of protein precipitated. S. B. S.

A Protein Substance in the Pancreatic Juice. ELKAN WECHSLER (*Zeitsch. physiol. Chem.*, 1910, 66, 284—286).—The protein in pancreatic juice is not a nucleo-protein, nor a gluco-protein. It gives Millon's and the biuret reactions. It contains 13·2% nitrogen. It yields in parts % of the total nitrogen: ammonia, 0·3, humin I, 10·9; humin II, 5·4; histidine, 4·1; arginine, 15·7; lysine, 1·3; and mono-amino-acids, 56·9. In parts % of the total protein, the following figures are given: arginine, 6·44; histidine, 1·99; lysine, 0·89; ammonia, 0·05. It is thus poor in lysine, and very poor in ammonia.
W. D. H.

Rate of Solution of Casein in Solutions of the Hydroxides of the Alkalis and of the Alkaline Earths. T. BRAILSFORD ROBERTSON (*J. Physical. Chem.*, 1910, 14, 377—392. Compare also Abstr., 1908, i, 930).—When casein is stirred at an approximately constant rate in solutions of the hydroxides of the alkalis or of the alkaline earths, the amount dissolved is given by the equation $x=kt^m$, where x is the number of grams of casein dissolved, t is the time which has elapsed since the casein was introduced into the solvent, and k and m are constants depending on the concentration and nature of the hydroxide solution and on the total mass of casein in the mixture.

Within the errors of experiment, the rapidity of solution is not affected by the temperature for temperatures ranging between room temperature and 30°.

Equally concentrated solutions of the hydroxides of potassium, sodium, lithium, and ammonium dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly, strontium hydroxide dissolving it the most, and barium hydroxide the least, rapidly.

The amount of casein dissolved by a solution of potassium hydroxide in a given time is directly proportional to the concentration of the hydroxide.

The velocity of solution of the casein increases with the mass of casein present in the mixture. The rate of increase of the velocity of solution with increasing mass of the casein is at first rather large, but it becomes much less as the mass of the casein is still further increased.

In the light of the above results, it is suggested that the factor which determines the rate of solution of casein in the alkaline solutions mentioned is the velocity with which the casein particles are penetrated and moistened by the solvent. T. S. P.

Partial Hydrolysis of Casein. ZDENKO H. SKRAUP and E. KRAUSE (*Monatsh.*, 1910, 31, 149—163. Compare Skraup and Hummelberger, Abstr., 1908, i, 711; Skraup and Woeber, *ibid.*, 1909, i, 446; Skraup and Lampl, *ibid.*, i, 537).—The products obtained by shaking casein with 60% sulphuric acid have been examined. It has been found possible to isolate a product very sparingly soluble in water, and resembling casein in many respects; this is termed albumose I. Among the products precipitated on the addition of ammonium sulphate, the one obtained when the solution is one-fourth saturated is formed in appreciable amount and is termed albumose II. A product which is not precipitated by ammonium sulphate is termed peptone. All three products were hydrolysed with concentrated hydrochloric acid, and the amounts of tyrosine and glutamic acid determined. The peptone did not yield any tyrosine, but the two albumoses gave somewhat larger yields than the casein itself. Albumose II gave far less glutamic acid than the original casein, whereas the peptone gave much the same amount, and albumose I somewhat more. The following colour-reactions of the three products were also examined: Millon's, glyoxylic acid, biuret, β-naphthol, and thymol. J. J. S.

Cleavage Products obtained by the Partial Hydrolysis of Proteins. EMIL ABDERHALDEN and AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, **66**, 13—18).—From Canton silk, glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride were obtained. From Neuchang silk and Indian tussore, *d*-alanine anhydride and glycyl-*d*-alanine anhydride were obtained. By the partial hydrolysis of Italian grège and Canton silk, alanine anhydride was not obtained.

W. D. H.

Blood Colouring Matter. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1910, **66**, 165—249. Compare this vol., i, 210).—Dehydrochloridehæmin undergoes changes on keeping which hinder the simple addition of hydrogen chloride and reformation of hæmin. Hæmin crystals are obtained from dehydrochloridehæmin by the action of hydrochloric acid, but hæmatin prepared by the action of alkalis on hæmin does not behave similarly. Hæmin dissolves both in aniline and in *p*-toluidine, owing to salt formation, but not in *o*-toluidine; this is ascribed to steric hindrance.

In the preparation of hæmatoporphyrin any oxidation in acid solution is to be avoided, and therefore sulphuric or hydrochloric acid should not be used. The iron eliminated is tervalent. Hæmin is more resistant to acids than hæmatin or dehydrochloridehæmin. Acetic acid acts but weakly on hæmatin, even at high temperatures.

Hæmin and hæmatin are insoluble in acid carbonates and diacid phosphates; with normal carbonates, acid carbonates are formed. The disodium salt of hæmatin gives up a molecule of sodium hydroxide on prolonged dialysis. Solutions of the alkali salts of hæmatin polymerise on keeping.

Precipitates obtained with metallic salts have not the exact composition: $C_{34}H_{30}O_4MN_4FeOH$. In the iron and silver salts, the metal seems to be fixed in a complex salt, and in such salts the attachment of the iron in hæmatin is rendered looser.

Typical hæmin is not obtained by Eppinger's method, and only in admixture with another substance by Sievert's method. The longer hæmatin remains in alkaline solution, the more difficult it is to prepare typical hæmin from it. The solution of hæmatin obtained by decomposing the barium compound with sulphuric acid and alcohol, when treated with hydrochloric acid at 50—72° gives a product soluble in alkali, but at 80° an insoluble product partly esterified is produced.

In hæmin the group $>$FeCl, in hæmatin $>$FeOH, replace the imide hydrogen of the pyrrole ring; the acid properties of the two substances are due to the presence of two carboxyl groups. In passing into dehydrochloridehæmin, hydrogen chloride is eliminated between one of these and the group $>$FeCl. In the reduction of hæmatin to hæmochromogen, ferric are reduced to ferrous compounds. The addition of carbon dioxide to hæmochromogen, or of oxygen, carbon dioxide or nitrous oxide to hæmoglobin, takes place at the iron. E. F. A.

The Non-Existence of "Protagon" in the Brain. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Biochem. Zeitsch.*, 1910, **25**, 151—160).—The authors maintain, in opposition to Wilson and

Cramer, that the so-called "protagon" is not a simple substance. A product can be obtained which on repeated recrystallisation from small quantities of alcohol does not vary very appreciably in composition; if, however, larger quantities of alcohol or other solvents be employed for recrystallisation, the "protagon" can be separated into fractions of varying composition, especially as regards the phosphorus content (from 0·07 to 3·13%). The authors give some details as to the composition of fractions obtained in various recrystallisations.

S. B. S.

Some Colloid-Chemical Aspects of Digestion with Ultramicroscopic Observations. Jerome Alexander (*J. Amer. Chem. Soc.*, 1910, **32**, 680—687).—After drawing attention to the fact that the catalytic action of enzymes probably depends on the preliminary formation of a compound of the enzyme with the substrate, it is pointed out that this product is most likely a colloidal absorption compound, and it is suggested that enzymes produce their effects by virtue of their specific surface actions and the motion of their particles. This view has been confirmed by observations with the ultramicroscope. When starch grains were treated with a solution of diastase, ultramicrons in rapid motion were seen to accumulate about the starch grains, which after a time showed an indented outline. The bright appearance of the field indicated the presence of numerous finer particles, whilst some particles of an intermediate size were visible. A solution of egg-albumin which had been heated nearly to boiling was opalescent, and, when viewed with the ultramicroscope, presented a field full of bright and rapidly moving ultramicrons. On adding a pepsin solution containing 15% of alcohol, immediate coagulation took place. On addition of dilute hydrochloric acid, the coagulated masses became disintegrated, and ultramicrons again appeared as before. The albumin particles gradually decreased in size, and eventually disappeared.

Reference is made to the action of reversible colloids in protecting irreversible or unstable colloids from coagulation, and consequently enabling colloidal sols to pass through membranes otherwise impermeable to them. This principle of colloidal protection has been demonstrated with the aid of the ultramicroscope. The casein particles in milk are seen to be in active motion, but if dilute acid is added, they immediately coagulate. If, however, a little gelatin or gum arabic is introduced before acidifying, coagulation is prevented, and the casein particles continue in motion. Gelatin exerts a greater protective action than gum, and is able to protect casein from coagulation by rennin.

E. G.

The Fatal Temperature for Plant Tyrosinases. Gabriel Bertrand and M. Rosenblatt (*Compt. rend.*, 1910, **150**, 1142—1145; *Bull. Soc. chim.*, 1910, [iv], **7**, 557—561. Compare Abstr., 1907, i, 811).—The view that more than one specific tyrosinase exists gains support from the fact that some enzymes of this type are more resistant to heat than others. The temperature at which the enzyme ceases to be capable of developing a coloration with tyrosine

has been determined for a number of preparations of different origin. Thus the fatal temperature for the tyrosinase from *Amanita rubescens* is 60—65°; from *Russula queletti*, *R. rubra*, and *R. delica*, 65—70°; from lentils and potatoes, 80—85°, and for that from the root of beetroot, 90—95°. The temperature for any particular enzyme is only slightly influenced by the nature of the solvent and the mode of preparation; furthermore, in mixtures containing more than one, each diastase behaves as if the others were absent. W. O. W.

Action of Hypophosphorous Acid on Dinaphthapyranol. Dinaphthapyrylphosphinous Acid. ROBERT FOSSE (*Bull. Soc. chim.*, 1910, [iv], 7, 357—359).—Dinaphthapyrylphosphinous acid, the formation of which has been described already (this vol., i, 292), forms small, white crystals, which develop a superficial reddish-violet coloration, and in alcoholic solution reduces silver nitrate. The *sodium* salt forms brilliant silvery crystals from water, which become opaque on drying, and gradually develop a reddish-violet tint. The *barium* salt separates in crystals from hot water. T. A. H.

Preparation and Properties of *p*-Iodophenylarsinic Acid and Certain of its Derivatives. I. EFISIO MAMELI and ALDO PATTA (*Gazzetta*, 1910, 40, i, 128—137).—Part of the work here described has been already published (Abstr., 1909, i, 543).

p-*Iodophenylarsenious oxide*, $C_6H_4I{\cdot}AsO$, obtained, together with hydriodic acid, by the action of water or an alkali carbonate or hydroxide on *p*-iodophenylarsenious iodide (*loc. cit.*), forms a straw-coloured powder, m. p. 245—250°.

p-*Di-iodoarsenobenzene*, $C_6H_4I{\cdot}As{:}As{\cdot}C_6H_4I$, prepared by reducing *p*-iodophenylarsinic acid by means of phosphorus acid, is a yellow substance, m. p. 145—150°, insoluble in all organic solvents.

T. H. P.

Preparation of Homologues of *p*-Aminophenylarsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 219210).—In the well-known preparation of magenta by heating *o*- and *m*-toluidines with arsenic acid, the latter acts simply as an oxidising agent; the methods are now described by which it is induced to become a substituting agent.

o-Toluidine (90 parts) is heated in a distilling apparatus, and finely-powdered arsenic acid (24 parts) slowly stirred in, the temperature being maintained with continual stirring at 165—168° during about an hour, when water and *o*-toluidine distil over; the internal temperature is then raised to 185—190° during an equal period, the apparatus cooled, and the contents treated with water, rendered alkaline with calcium or barium hydroxide, and any residual toluidine removed with steam. The liquid is saturated with sodium chloride, and, after twenty-four hours, filtered, and the liquid just acidified with hydrochloric acid, when a resinous by-product separates, and, after a further twenty hours, the pure 4-*amino*-3-*tolylarsinic acid* is precipitated in needles, m. p. 194—195°. The *sodium* salt is crystalline, and can be separated from its aqueous solution by addition of alcohol.

4-*Amino-2-tolylarsinic acid*, m. p. 180°, is similarly prepared from *m*-toluidine.

4-*Amino-2 : 5-xylylarsinic acid*, from *p*-xylidine, crystallises with $1H_2O$, and when anhydrous has m. p. 215°. These compounds are colourless, and are readily soluble in hot, sparingly in cold, water; they yield crystalline salts, and diazotise readily with nitrous acid; their therapeutic germicidal action is analogous to that of *p*-aminophenylarsinic acid. F. M. G. M.

Action of Organo-magnesium Compounds on Boron Trichloride, Sulphur Chloride, and on the Chloride and Esters of Sulphurous Acid. WILHELM STRECKER (*Ber.*, 1910, **43**, 1131—1136).—When magnesium phenyl bromide reacts with boron trichloride, only one chlorine atom is replaced, so that the final product is always phenylboric acid (compare Khotinsky and Melamed, Abstr., 1909, i, 864). This acid cannot be titrated in the ordinary way, but it is more dissociated than boric acid, the molecular conductivity at 25° being 0·133. On the assumption that the conductivity at infinite dilution is the same as that of benzoic acid, this gives a degree of dissociation of 0·00027 at 25°, while that of boric acid is 0·00012 (Walker and Cormack, Trans., 1900, **77**, 5).

Magnesium phenyl bromide reacts with sulphur chloride (S_2Cl_2), yielding phenyl disulphide; diphenyl is also formed.

As a result of the action of magnesium phenyl bromide and magnesium benzyl bromide on thionyl chloride, the corresponding sulphoxides are formed, in addition to diphenyl and benzyl sulphide. With *s*-diethyl sulphite the same sulphoxides are obtained. *as*-Diethyl sulphite and magnesium phenyl bromide yield phenyl ethyl sulphone.

The action of magnesium ethyl iodide and magnesium phenyl bromide on benzene solutions of nitrogen chloride (Hentschel, Abstr., 1897, ii, 447) was tried without result. R. V. S.

Action of Thionyl Chloride on Organo-magnesium Compounds. VICTOR GRIGNARD and L. ZORN (*Compt. rend.*, 1910, **150**, 1177—1179. Compare Strecker, preceding abstract).—Thionyl chloride resembles carbonyl chloride in its action on organo-magnesium compounds (Abstr., 1903, i, 455). When 1 mol. of the chloride is employed with 2 mols. of an aromatic magnesium compound, a sulphinone is produced, whilst if a greater proportion (3 mols.) of the magnesium derivative is taken, a sulphonium complex, of the type $SR_3{\cdot}OMgX$, is formed. When X is an aliphatic radicle, this undergoes decomposition in two directions: (1) $SR_3{\cdot}OMgX = SR_2 + MgX{\cdot}OR$; (2) $SR_2(OMgX){\cdot}C_nH_{2n+1} = SR_2 + MgX{\cdot}OH + C_nH_{2n}$.

From the magnesium derivative of bromoquinol dimethyl ether, a small quantity of bis-2 : 5-dimethylphenylsulphinone, $[C_6H_3(OMe)_2]SO$, was obtained, in the form of small crystals, m. p. 124—125°. W. O. W.

Organic Chemistry.

Purification and the Physical Constants of Some Organic Liquids. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1910, **24**, 244—268).—The author gives a general discussion of the precautions which are necessary in the purification of an organic liquid by fractional distillation. Twenty-five different compounds have been investigated, the criteria of purity being the boiling point and the density. In some cases the freezing point and the critical solution temperature in an inert solvent were also used as criteria.

The following table gives a summary of the results. In each case the ± refers to variations in the last decimal place given.

Substance.	B. p. /760 mm.	dt/dp for 10 mm.	$D_{4^\circ}^{0^\circ}$.
*iso*Pentane	27·95°±1	0·37°	0·63942±3
Ethyl bromide	38·40 ±1	0·36	1·50138±2
Ethylene dichloride	83·70 ±1	—	1·28238±2
Chloroform	61·20 ±1	0·35	1·52635±2
Carbon tetrachloride	76·75 ±1	0·44	1·63255±2
Carbon disulphide	46·25 ±1	0·42	1·29272±2
Acetonitrile	81·60 ±1	0·30	0·80350±1
Ethylamine	16·55 ±1	0·28	0·70570±10
Methyl alcohol	64·70 ±1	0·30	0·81017±3
Ethyl ether	34·60 ±1	0·36	0·73627±3
Acetone	56·10 ±1	0·30	0·81249±3
Methyl ethyl ketone	79·60 ±2	0·38	0·82551±1
Methylal	42·30 ±2	0·40	0·88548±2
*iso*Butyric acid	154·35 ±2	0·32	0·96819±2
Methyl formate	31·75 ±2	0·34	1·00340±3
Ethyl acetate	77·15 ±1	0·41	0·90476±2
Ethyl propionate	99·10 ±1	0·40	0·91245±2
Toluene	110·70 ±1	0·42	0·88448±2
Chlorobenzene	132·00 ±1	0·49	1·12795±1
Bromobenzene	156·15 ±1	0·53	1·52193±1
Benzonitrile	191·30 ±1	0·54	1·02279±3
Nitrobenzene	210·85 ±1	0·48	1·22290±4
Aniline	184·40 ±1	0·51	1·03895±2
Anisole	153·80 ±2	0·48	1·01237±2
Pyridine	115·50 ±1	0·44	1·00302±2

T. S. P.

The First Synthesis of Ethyl Alcohol. RAPHAEL MELDOLA (*J. Soc. Chem. Ind.*, 1910, **29**, 737—740).—An historical paper in which the author maintains his thesis that Henry Hennel was the first to synthesise ethyl alcohol (compare Berthelot, Abstr., 1899, i, 471; Fritsche, 1902, i, 657). T. S. P.

Molecular Compounds of Alcohol and Water. T. FAWSSETT (*Pharm. J.*, 1910, [iv], **30**, 754—757).—This paper is largely the mathematical exposition of a theory proposed to explain the contraction occurring when ethyl alcohol and water are mixed. According to

the theory advanced, when ethyl alcohol and water combine the first compound formed is invariably $(C_2H_6O)_{18},H_2O$, which subsequently combines with successive molecules of water, forming an indefinite number of compounds. Further, that the formation of each molecular compound or "system" causes a definite contraction of the total volume, and that the contraction is proportional to the weight of the water in the equation: $(C_2H_5\cdot OH)_9,H_2O + H_2O = (C_2H_5\cdot OH)_9,2H_2O$. From the latter it is deduced that the contraction $\overset{(n)}{r}$ resulting on the formation of the compound $(C_2H_6O)_{18},nH_2O$ from the compound $(C_2H_6O)_{18},(n-1)H_2O$ is equal to $\{5\cdot136n/(23+n) - 5\cdot136(n-1)/[23+(n-1)]\}$ of the volume of water added. The contractions $\left(\overset{(n)}{r}\right)$ produced by nine successive additions of 5/18 gram-molecules of water to 5 gram-molecules of ethyl alcohol were measured at 15·5° in an apparatus described. The observed contractions diminish from 0·221 for the first addition to 0·113 for the ninth, the calculated figures varying from 0·214 to 0·119, whilst the difference only amounts to 0·01 in three instances. E. H.

αα-Dialkyl-β-keto-alcohols. EDMOND E. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1910, [viii], 20, 173—194).—Recapitulates work recorded already in Abstr., 1907, i, 749; 1908, i, 78, 248, 319, 596; 1909, i, 85, and continues the work dealt with in Abstr., 1909, i, 632. The following data are new. Kling and Viard's statement (Abstr., 1904, i, 545) that tertiary alcohols are dehydrated at the boiling point of naphthalene could not be verified in the cases of trimethylcarbinol or α-hydroxydi*iso*propyl ketone, $CHMe_2\cdot CO\cdot CMe_2\cdot OH$. The primary alcohol, *ethyl hydroxy*-sec.-*butyl ketone*, $OH\cdot CH_2\cdot CHEt\cdot COEt$, b. p. 102·5°/13 mm., is also stable under these conditions.

α-Hydroxydi*iso*propyl ketone, the formation of which has been described already (Abstr., 1908, i, 319), furnishes a p-*nitrophenylhydrazone*, m. p. 127·5°, crystallising in yellow needles. Attempts to synthesise this hydroxy-ketone from ethyl α-hydroxy-*iso*valerate by the action of magnesium methyl iodide resulted in the production of *βδ-dimethylpentane-βγ-diol*, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot OH$, m. p. 59°, which crystallises in colourless needles, and yields a *monoacetyl* derivative, $CHMe_2\cdot CH(OAc)\cdot CMe_2\cdot OH$, b. p. 88—89°/11 mm., and a *phenylurethane*, m. p. 127°. This glycol on oxidation with chromic acid gives a mixture of ketones, but no α-hydroxydi*iso*propyl ketone. On dehydration with sulphuric acid, the glycol yields di*iso*propyl ketone (Abstr., 1904, i, 219).

The following details are given of the compounds prepared in the course of the synthesis of ethyl tiglyl ketone (Abstr., 1908, i, 596): β-hydroxy-α-methylbutyric acid furnishes a *phenylurethane*, m. p. 128°, crystallising in slender needles. The acetyl derivative of the acid yields an *ethyl* ester, b. p. 97·5°/15 mm., a p-*toluidide*, m. p. 129°, slender needles, an α-*naphthylamide*, m. p. 126°, and an *acid chloride*, b. p. 84°/13 mm. The last-mentioned substance condenses with zinc ethyl iodide to give *β-acetoxy-α-methylpropyl ethyl ketone*,

$$OAc\cdot CHMe\cdot CHMe\cdot COEt,$$

b. p. 97—97·5°/14 mm., and this on hydrolysis in the cold furnishes a

mixture of the corresponding *hydroxy-ketone*, b. p. 89—90°/14 mm., and ethyl tiglyl ketone, b. p. 50·5°/13 mm.; the latter absorbs hydrogen bromide, but the bromo-compound formed is unstable, and could not be isolated. T. A. H.

Hydrogenation of Acetylenic Compounds. ROBERT LESPIEAU (*Compt. rend.*, 1910, **150**, 1761—1762).—Reduction of unsaturated glycols, such as the compound $OH\cdot CH_2\cdot C{:}C\cdot CH_2\cdot OH$ or

$$OH\cdot CH_2\cdot C{:}C\cdot C{:}C\cdot CH_2\cdot OH,$$

by means of platinum black and hydrogen in alcoholic or ethereal solution results in the production of a good yield of the corresponding saturated glycols. Small quantities of hexane and hexanol are also formed in the case of the latter compound. The yield is considerably diminished if the dimethyl ethers of the glycols are employed, owing to the formation of saturated hydrocarbons and of dimethyl ether.

W. O. W.

Hydroxydiacetyl. OTTO DIELS and MILAN FARKAŠ (*Ber.*, 1910, **43**, 1957—1962).—It has not been found possible to obtain a monobromo-derivative of diacetyl, the only product formed by direct bromination being the dibromo-derivative (compare Fittig, Keller, and Daimler, Abstr., 1889, 491). Diacetylmonoxime yields a monobromo-derivative when dissolved in methyl alcohol and treated with bromine at 0°, and this reacts with a methyl alcoholic solution of potassium acetate, yielding the corresponding acetyl derivative, which, when hydrolysed with barium hydroxide solution, yields the oxime of hydroxydiacetyl; but, so far, it has not been found possible to obtain hydroxydiacetyl itself.

Modifications of Diels and Jost's method (Abstr., 1902, i, 744) for the preparation of diacetylmonoxime are recommended. Its *bromo-derivative*, $CH_2Br\cdot CO\cdot CMe{:}N\cdot OH$, crystallises from benzene, has m. p. 83—84°, and attacks the mucous membrane. The *acetate*,

$$OAc\cdot CH_2\cdot CO\cdot CMe{:}N\cdot OH,$$

forms snow-white crystals, m. p. 93·5—94°. It yields a *phenylhydrazone*, $OAc\cdot CH_2\cdot C({:}N_2HPh)\cdot CMe{:}N\cdot OH$, which forms sulphur-yellow, dichroic crystals, m. p. 132—133° (corr.).

Hydroxydiacetylmonoxime, $OH\cdot CH_2\cdot CO\cdot CMe{:}N\cdot OH$, crystallises from water in large, brilliant prisms, m. p. 118·5—119·5° (corr., decomp.), and yields a *phenylhydrazone*, $OH\cdot CH_2\cdot C({:}N_2HPh)\cdot CMe{:}N\cdot OH$, which crystallises from alcohol in long, pale yellow, refractive needles, m. p. 197·5° (corr.).

Hydroxydiacetylosazone, $OH\cdot CH_2\cdot C({:}N_2HPh)\cdot CMe{:}N_2HPh$, obtained by the action of an excess of phenylhydrazine on a dilute acetic acid solution of the monoxime, crystallises in golden-yellow plates, m. p. 189° (corr., decomp.) J. J. S.

Attempts to Transform Nitrous Vapours into the Corresponding Calcium Salts by the Use of Ethyl Nitrite and Nitrate. EUGÈNE TASSILLY and J. LEROIDE (*Bull. Soc. chim.*, 1910, [iv], **7**, 622—628).—Nitrous vapours are absorbed fairly completely by ethyl alcohol with the formation of ethyl nitrite and nitrate, but the resulting solution on treatment with lime does not furnish good

yields of the corresponding calcium salts, so that this method cannot be used for the conversion of waste nitrous fumes into calcium salts of industrial value.

Nitric oxide, obtained by the action of nitric acid on copper, was mixed with air, previously purified by passing over (1) pumice stone mixed with potassium hydroxide, and (2) pumice stone saturated with sulphuric acid, to form a mixture containing 1 to 2% of nitrous fumes, and this was drawn through alcohol kept at $-20°$, then through glass wool at $-35°$ to $-40°$, to eliminate alcohol, etc, from the issuing gas, and finally through a tube containing diphenylamine in sulphuric acid. The last tube served as a test for nitrous vapours in the issuing gas, and its subsequent examination showed that the proportion of nitrous vapours which escaped absorption was less than 1×10^{-5} of that dissolved by the alcohol. The alcoholic solution at first contains ethyl nitrite and ethyl nitrate, but, when kept, part of the nitrate is hydrolysed, and the nitric acid formed reacts with the excess of alcohol to form acetaldehyde. Experiments on the hydrolysis of ethyl nitrite and nitrate in alcohol with potassium hydroxide showed that good yields of the potassium salts could be obtained, but with lime under similar conditions the hydrolysis of ethyl nitrite is negligible at atmospheric temperature or 100°, but amounts to 23·1% at 140°, and with ethyl nitrate amounts to 29·0 and 55·0% at 140° and 150° respectively. Potassium is not displaced from potassium nitrite or nitrate by boiling with lime in presence of alcohol. T. A. H.

Ethyl Metaphosphate and its Use in Organic Chemistry. KURT LANGHELD (*Ber.*, 1910, **43**, 1857—1860).—*Ethyl metaphosphate*, $C_2H_5PO_3$, can be prepared by the action of ethyl iodide on silver metaphosphate, but is more readily obtained by the action of phosphoric oxide on anhydrous ethyl ether, $OEt_2 + P_2O_5 = 2EtPO_3$. It forms a thick syrup, and may be purified by solution in chloroform and precipitation with ether. It is readily hydrolysed by alkalis, and when boiled with ethyl alcohol gives a mixture of di- and tri-ethyl phosphates.

The metaphosphate when boiled with chloroform and dextrose yields two organic phosphorus compounds, from which crystalline barium salts have been obtained.

Leucine reacts with a chloroform solution of ethyl metaphosphate, yielding the compound: $PO(OEt)(OH)\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CHMe_2$.

The metaphosphate is a good condensing agent, as it eliminates water or ammonia very readily from mixtures of organic compounds. J. J. S.

Formation and Decomposition of Thiols; Synthesis of Dialkyl Sulphides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, **150**, 1569—1572. Compare this vol., i, 456).—Attempts have been made to improve the yield of thiols from secondary alcohols when these are submitted to the catalytic process already described. Substitution of the oxides of zirconium, uranium, tungsten, chromium, molybdenum, or aluminium for the thorium oxide previously employed resulted in diminished yields in the case of *iso*amyl alcohol and of phenol.

Metallic sulphides have a catalytic effect on thiols precisely similar to that exercised by alumina on alcohols, and if cadmium sulphide is used, the reaction affords a convenient method for the preparation of dialkyl sulphides. When passed over this substance at 320—330°, ethyl hydrogen sulphide is converted into diethyl sulphide, whilst at 380° decomposition into ethylene and hydrogen sulphide occurs. With secondary thiols, the yield of dialkyl sulphide is smaller, and the tendency to undergo decomposition more marked. The reaction is represented as (1) $CdS + 2C_nH_{2n+1}\cdot HS = Cd(S\cdot C_nH_{2n+1})_2 + H_2S$; (2) $Cd(S\cdot C_nH_{2n+1})_2 = CdS + (C_nH_{2n+1})_2S$. W. O. W.

Basic Ferric Acetate Contained in the Former Official Solution of Ferric Acetate. RUDOLF F. WEINLAND (*Arch. Pharm.*, 1910, **248**, 337—345).—The addition of sodium platinichloride in slight excess to the former official solution of ferric acetate of the D.A.-B. III causes a precipitation of the orange-red platinichloride, $\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]\frac{1}{2}PtCl_6,5H_2O$, described previously (Abstr., 1909, i, 872). The basic acetate in the official solution, therefore, is the monoacetate, $\left[Fe_3\begin{matrix}(OAc)_6\\(OH)_2\end{matrix}\right]OAc$. C. S.

Colloidal Properties of Soluble Soaps. FILIPPO BOTAZZI and C. VICTOROFF (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 659—665).—The soap employed consisted chiefly of sodium oleate with smaller quantities of palmitate, stearate, etc. When a concentrated solution of it is dialysed, the volume of liquid in the dialyser at first increases, and the clear solution becomes opalescent and finally milky. This is due to the gradual hydrolysis of the soap; the alkali formed diffuses out, and fatty acids and acid soaps are precipitated. At the end of the dialysis, the liquid forms three layers, two, at the surface and at the bottom respectively, consisting of the acids and the acid soaps, and a third, intermediate, milky layer, which is a microgranular suspension of these substances in a very dilute solution of soap. A small quantity of soap is also lost by diffusion during the dialysis. When examined electrically, both the soap and the granules in the dialysed liquid are found to move towards the anode. On adding water or small quantities of $N/10$-sodium hydroxide to the concentrated soap solution, a gradual decrease of the viscosity occurs. When $N/10$-sodium hydroxide is added to the turbid, filtered liquid after dialysis, the viscosity at first increases, then decreases to its former value. If water is now added, the viscosity again slowly rises, owing to the decrease in concentration of the alkali present. The addition of an excess of sodium hydroxide causes precipitation of the soap. The concentrated soap solution has a very low surface tension, whilst that of the liquid after dialysis is not much less than that of distilled water. The variation of surface tension caused by addition of sodium hydroxide is similar to the changes produced in the viscosity, but in the reverse direction; when the viscosity increases the surface tension diminishes, and vice versa. R. V. S.

Hydrolytic Decomposition of Aqueous Alcoholic Solutions of Alkali Soaps. DAVID HOLDE [with H. DÖSCHER and G. MEYERHEIM] (*Zeitsch. Elektrochem.*, 1910, **16**, 436—442).—When a solution of a soap in aqueous alcohol is made exactly neutral to phenolphthalein and then shaken with a solvent such as benzene, the solution becomes red and the benzene contains some of the fatty acid of the soap, showing that the neutral solution is hydrolysed to some extent. The hydrolysis diminishes as the concentration of the alcohol increases, and practically disappears in 80% alcohol. The bearing of this on the accuracy of titrations of fatty acids is discussed.

The partition of oleic acid between "benzine" and aqueous alcohol is also studied. With 40% alcohol, 99·8% of the acid passes into the "benzine." T. E.

Carbohydrate Esters of Higher Fatty Acids. W. R. BLOOR (*J. Biol. Chem.*, 1910, **7**, 427—430. Compare Neuberg and Pollak, this vol., i, 157).—Mannitol has been condensed with stearic acid under the influence of concentrated sulphuric acid at 65—75°, the mixture being then cooled and ether added (Grün's method).

A certain amount of ethyl stearate is formed as a by-product, and this complicates the purification of the condensation product. After repeated precipitation from its methyl alcoholic solution, *mannide distearate*, $C_6H_8O_2(C_{18}H_{35}O_2)_2$, was obtained as a colourless, semi-translucent, amorphous mass, which crystallised from ether in microscopic needles, m. p. 51°. It has $[\alpha]_D^{20}$ +63·9°, and is readily hydrolysed by alcoholic sodium hydroxide solution. J. J. S.

Ester Condensation: Ethyl Oxalate and Propionitrile. WILHELM WISLICENUS and WILHELM SILBERSTEIN (*Ber.*, 1910, **43**, 1825—1836).—The ordinary Claisen condensation (ethyl acetoacetate formation) is termed *ester condensation.* Three factors are of importance: the ester, the methylene derivative, and the condensing agent. According to Claisen the ester first forms an additive compound with the sodium alkyloxide. The most reactive ester is ethyl oxalate, then follow ethyl formate, nitrite, acetate, benzoate, and nitrate. The most reactive methylene compounds are benzyl cyanide, ketones, ethyl acetate, fluorene, etc. Freund and Speyer (Abstr., 1902, i, 584) have found that sodamide is a more effective condensing agent than sodium ethoxide. The authors recommend the use of potassium ethoxide in cases where sodium ethoxide gives but poor yields or produces no condensation at all; thus ethyl oxalate and propionitrile do not condense in the presence of sodium ethoxide (Fleischhauer, Abstr., 1893, 397), but with potassium ethoxide in the presence of anhydrous ether give an 83% yield of ethyl β-cyano-α-ketobutyrate after the mixture has been kept for three days at the ordinary temperature. The *potassium* compound, $C_7H_8O_3NK$, crystallises from alcohol in slender, colourless prisms, m. p. 162—163°, when freshly prepared. The salt is stable, is not hygroscopic, and is not decomposed by carbonic or acetic acids. The *sodium* salt is less soluble, and the *silver* and *copper* salts form precipitates. *Ethyl β-cyano-α-ketobutyrate*, $CN{\cdot}CHMe{\cdot}CO{\cdot}CO_2Et$, crystallises from benzene

in large, yellow prisms, m. p. 66—67° and b. p. 123°/17 mm. It dissolves to an appreciable extent in water, yielding acid solutions. When freshly liberated from its potassium salt, the ester gives a pale coloration with alcoholic ferric chloride, but the coloration increases with the time. This points to the liberation of the ketonic form and its gradual passage into the enolic form: $CN{\cdot}CMe{:}C(OH){\cdot}CO_2Et$.

The *ammonium* salt, $C_7H_{12}O_3N_2$, forms colourless crystals, m. p. 113—114°.

A 20% yield of *β-cyano-a-ketobutyric acid* (propionitrileoxalic acid), $CN{\cdot}CHMe{\cdot}CO{\cdot}CO_2H$, can be obtained by dissolving the ester in ether and a little alcohol, and passing in hydrogen chloride and shaking with a little water. It forms yellow needles, m. p. 207—208°.

When hydrolysed with 20% aqueous potassium hydroxide, the ester yields propionic and oxalic acids (acid hydrolysis), but when hydrolysed with 25% sulphuric acid the product is propionylformic acid, m. p. 151—152° (compare Wislicenus and Arnold, Abstr., 1888, 361) (ketonic hydrolysis).

When warmed with dilute potassium hydroxide at 40°, or when treated with alkaline hydrogen peroxide at 40° (Radziszewski's method), the ester yields *oxalpropionamide*, $NH_2{\cdot}CO{\cdot}CHMe{\cdot}CO{\cdot}CO_2H$; this is best isolated as its *phenylhydrazone*, $C_{11}H_{13}O_3N_3$, which crystallises in glistening, colourless plates, m. p. 171—172°.

An 87% yield of the *anil*, $CN{\cdot}CHMe{\cdot}C(CO_2Et){:}NPh$, is obtained by gently warming the ester with aniline; it crystallises from ether in yellow, flat plates, m. p. 115—116°. If the mixture is heated for some time, aniline oxalate is formed.

The ester yields an *oxime*, $CN{\cdot}CHMe{\cdot}C({:}N{\cdot}OH){\cdot}CO_2Et$, in the form of colourless prisms, m. p. 104—105°, and a *phenylhydrazone*,

$$CN{\cdot}CHMe{\cdot}C(CO_2Et){:}N_2HPh,$$

in the form of yellow plates, m. p. 124—126°. The phenylhydrazone, when heated gradually to 200°, undergoes molecular rearrangement, and yields an isomeric *compound*, m. p. 109—111°, which is probably a pyrazole derivative, $NPh<\begin{matrix}C(NH_2){:}CMe \\ N{=\!=\!=}C{\cdot}CO_2Et\end{matrix}$.

The ester reacts with an alcoholic solution of hydrazine hydrate, yielding the *hydrazone* of *β-cyano-a-ketobutyrohydrazide*,

$$CN{\cdot}CHMe{\cdot}C({:}N_2H_2){\cdot}CO{\cdot}NH{\cdot}NH_2,$$

which crystallises in colourless prisms, m. p. 190—192°.

When brominated in chloroform solution, the ester yields *ethyl β-bromo-β-carboxylamido-a-ketobutyrate*, $NH_2{\cdot}CO{\cdot}CMeBr{\cdot}CO{\cdot}CO_2Et$, which crystallises in colourless, slender prisms, m. p. 134—135°.

The potassium derivative of ethyl β-cyano-a-ketobutyrate, when boiled for several days with alcoholic ethyl iodide, yields *ethyl β-cyano-β-methyl-β-ethylpyruvate* (*ethyl β-cyano-a-keto-β-methylvalerate*),

$$CN{\cdot}CMeEt{\cdot}CO{\cdot}CO_2Et,$$

as a colourless oil, b. p. 130°/24 mm., which yields a-methylbutyric acid when hydrolysed with potassium hydroxide solution and methylethylpyruvic acid when hydrolysed with dilute sulphuric acid. The phenylhydrazone of the pyruvic acid has m. p. 132—133° (compare Locquin, Abstr., 1906, i, 929).

A cold solution of diazobenzene chloride reacts with the potassium salt of ethyl β-cyano-α-ketobutyrate, yielding the phenylhydrazone of acetyl cyanide (Favrel, *Bull. Soc. chim.*, 1902, [iii], **27**, 194). The potassium salt reacts with *p*-nitrobenzoyl chloride, yielding the p-*nitrobenzoyl* derivative, $CN\cdot CMe:C(CO_2Et)\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, as colourless plates, m. p. 83—84°, which are readily hydrolysed.

J. J. S.

Cork. III. MAX VON SCHMIDT (*Monatsh.*, 1910, **31**, 347—356. Compare Abstr., 1904, i, 501).—It has been shown previously that the extract of cork meal in chloroform or other indifferent solvent contains cerin and about 10% of glycerides, and that about 30% of fatty acids, but no glycerides, are obtained by heating the residue with alcoholic potassium hydroxide; hence the fatty acids in cork are not present as glycerides and are insoluble. Since they cannot be combined with the cerin, which would be found in the alcoholic solution if such were the case, it follows that they must be present as anhydrides or as insoluble polymerides. This conclusion is justified by experiments on phellonic acid—the acid obtained from cork which has been examined most thoroughly. When this acid is heated for fifty-four hours at the b. p. of xylene, or for six hours with fuming hydrochloric acid in a water-bath, it is converted into an *anhydride*, m. p. 102°, which, however, is soluble in chloroform and in benzene; hence this anhydride is probably present in cork, its non-extraction by chloroform being due to the fact that it is embedded in the insoluble constituents of the cork. If this is so, the crude fatty acids obtained from cork should yield an insoluble product by heating. Experiment proves this, for at 140° the crude acids are converted into a brown, elastic, transparent mass, which is insoluble in indifferent solvents and is impermeable by gases. In fact, by heating a mixture of the crude acids and an equal weight of sawdust at 140°, a product is obtained which closely resembles natural cork in colour, elasticity, and workability and other properties, and differs from it only by the absence of its characteristic structure.

The substance to which the conversion of these fatty acids into an insoluble form is chiefly due is suberic acid, which is converted by heating, without loss of water and in the absence of air, into an insoluble, elastic mass, probably of a polymeride.

Cork, therefore, consists of an insoluble mixture of anhydrides and polymerides of solid and liquid fatty acids, together with the glycerides of these acids. Young cork most probably contains only glycerides, which in course of time, under the influence of air, light, and probably also of enzymes, are hydrolysed, the glycerol being oxidised to carbon dioxide and water; the fatty acids partly polymerising and partly forming anhydrides.

C. S.

Complex Iridium Derivatives. Iridiodichlorodinitro-oxalates. MAURICE VÈZES and ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1910, [iv], **7**, 507—512. Compare *Proc. verb. Soc. Sci. Bordeaux,* July 18, 1901).—*Tripotassium iridiodichlorodinitro-oxalate,*

$$K_3IrCl_2(NO_2)_2C_2O_4,2H_2O,$$

obtained by boiling potassium iridiodichloro-oxalate (Abstr., 1909, i, 762) in concentrated aqueous solution with potassium nitrite, crystallises in orthorhombic, orange-yellow needles ($a:b:c = 0.59101:1:0.81461$). It is stable at ordinary temperatures, loses $2H_2O$ and becomer yellow at 100—120°, evolves nitrous fumes at 250°, and decomposes completely at 275°, leaving a black residue having the shape of the original crystals and consisting of iridium, potassium chloride, and potassium nitrite. No deflagration occurs. The salt does not give reactions for chloride, nitrite, or oxalate.

The *silver* salt obtained by interaction between solutions of the potassium salt and of silver nitrate, the latter in excess, crystallises in anhydrous, microscopic, birefringent, bright yellow lamellæ of rhombic form and having an acute angle 65°. The crystals give extinction with crossed nicols in a direction oblique to the diagonal. The salt is stable even above 100°, but begins to turn brown at 120°, and decomposes completely at 260°, but does not deflagrate. It undergoes double decomposition with hydrochloric acid or chlorides.

T. A. H.

Complex Derivatives of Iridium. Iridiodichlorodinitro-oxalic Acid and Salts. ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1910, [iv], 7, 512—516).—The acid could not be isolated, but was obtained in solution by adding the equivalent amount of hydrochloric acid to the silver salt (see preceding abstract). This solution on evaporation even under reduced pressure evolved nitrous fumes, leaving eventually a black residue containing iridium. Salts of this acid can be prepared by (1) double decomposition with the potassium salt; (2) action of chlorides on the silver salt, or (3) by neutralisation of the aqueous solution of the acid. The salts have generally the properties recorded already for the potassium and silver salts (*loc. cit.*). They are very soluble in water, with the exception of the silver and thallous salts. Salts of the following metals were prepared: *Rubidium*, *cæsium*, *thallium*, *ammonium*, *lithium*, and *sodium*. The last three crystallise with $2H_2O$. The hydrated ammonium salt is unstable and loses its water at atmospheric temperatures when kept over sulphuric acid, and some anhydrous crystals isomorphous with those of the rubidium salt separate with the hydrated salt in preparing the latter. The ammonium salt also differs from the others in deflagrating when heated.

T. A. H.

By-Products Obtained During the Replacement of the Alkyl Groups in Ethyl Malonate. TELEMACHOS KOMNENOS (*Monatsh.*, 1910, 31, 421—438).—It has been shown (this vol., i, 361) that methyl ethanetetracarboxylate is the chief product obtained by the addition of iodine to the reaction product of ethyl malonate and sodium methoxide. The oily product of the reaction has now been examined. The portion which solidifies after a few days' keeping is probably *methyl acetone-ααγ-tricarboxylate*, $CH(CO_2Me)_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$, m. p. 105—108° (*phenylhydrazone*, m. p. 125°), although its properties are not analogous to those of the ethyl ester described by Willstatter. The alcoholic mother liquor of the preceding ester contains a small quantity of

another *substance*, $C_9H_{12}O_7$, m. p. 120°, not identical with, but possibly the enolic form of, the preceding ester, and also a *substance*, $C_{12}H_{16}O_9$, m. p. 75° (*phenylhydrazone*, m. p. 108—110°), which is probably *methyl γ-hydroxyhexan-βδ-dione-ααε-tricarboxylate*, formed by the elimination of 2 mols. of methyl alcohol and 1 mol. of carbon dioxide from 2 mols. of methyl malonate and 1 mol. of methyl tartronate (which is produced by the action of iodine and water on methyl sodiomalonate).

The remaining oily portion of the original by-product is found to consist chiefly of an *ester*, $C_9H_{12}O_7$, m. p. 97° (*phenylhydrazone*, m. p. 117—120°), which is isomeric, but not identical, with the ester first mentioned; it also contains an *ester*, $C_{14}H_{18}O_{11}$, m. p. 85—87°, which is probably *methyl butan-γ-one-ααβδδ-pentacarboxylate*, and also a very small quantity of an *ester*, $C_{12}H_{16}O_8$, m. p. 85° (*phenylhydrazone*, m. p. 110°), which is possibly *methyl hexan-βδ-dione-αγε-tricarboxylate*.

It is noteworthy that all the products obtained from ethyl malonate in the reaction under examination are methyl esters.

C. S.

Acidity of Derivatives of Ethyl Oxalacetate. HENRI GAULT (*Compt. rend.*, 1910, **150**, 1608—1610).—The ethyl esters of the following acids may be titrated by alkalis, using phenolphthalein as indicator, in cold alcoholic or acetone solutions; the results obtained enable the molecular weights to be determined with a fair degree of accuracy: oxalacetic, oxalosuccinic, α-oxaloglutaric, methylenebisoxalacetic, ethylidenebisoxalacetic, propylidenebisoxalacetic, heptylidenebisoxalacetic, *cyclo*pentan-βγ-dione-αδ-dicarboxylic, and the corresponding αε-di- and αδε-tri-carboxylic acids. The molecular weights thus determined agree with the accepted constitutions for these substances, but in the case of methyloxalosuccinic and α-oxalotricarballylic esters, the results are abnormally high.

W. O. W.

Acidic Character of Ethyl Oxalacetate. LOUIS JACQUES SIMON (*Compt. rend.*, 1910, **150**, 1760. Compare Abstr., 1904, i, 648; 1907, i, 963).—The author has already called attention to the acidic character of ethyl oxalacetate recently studied by Gault (preceding abstract).

W. O. W.

Decomposition of Formaldehyde at a Red Heat. ARMAND GAUTIER (*Compt. rend.*, 1910, **150**, 1725—1726. Compare this vol., ii, 607).—When a mixture of hydrogen and formaldehyde is passed through a porcelain tube heated to redness, the formaldehyde is decomposed in accordance with the equation: $CH_2O = CO + H_2$. If passed over iron at 650°, the gaseous product contains in addition 0·8% of methane.

W. O. W.

Electro-syntheses. V. SIMA M. LOSANITSCH (*Ber.*, 1910, **43**, 1871—1874. Compare this vol., i, 1).—Methylal, when subjected to the silent electric discharge, yields carbon monoxide, methane, hydrogen, a small amount of unsaturated hydrocarbons, and large

quantities of aldehydes, which are polymerides of formaldehyde and acetaldehyde, namely, $C_3H_8O_3$, $C_7H_{18}O_6$, $C_8H_{18}O_5$, and $(C_3H_6O_2)_n$.

Acetal yields aldehyde compounds: $C_6H_{12}O_2$, b. p. 100—110°/16 mm.; $C_{16}H_{30}O_5$, b. p. 140—200°/16 mm., and $C_{14}H_{22}O_4$.

Methyl sulphide yields the compounds $C_5H_{12}S_4$, b. p. 45—50°/14 mm.; $C_7H_{16}S_5$, b. p. 80—90°/14 mm.; $C_5H_{12}S_4$, b. p. 120—140°/14 mm., and $C_7H_{14}S_6$, which are polymerides of formaldehyde and thioacetaldehyde.

*iso*Pentane and ammonia yield an oily *hydrocarbon*, C_nH_{2n}, and a *base*, $C_6H_{13}N$, which has b. p. 90—95°/14 mm.

Ether and ammonia yield a *base*, $C_9H_{17}ON_3$. J. J. S.

Injurious Action of the Sun's Rays on Acetone. BATIK (*Chem. Zeit.*, 1910, **34**, 735).—When acetone is exposed to the direct rays of the sun, it is affected in such a way that it almost immediately decolorises permanganate. When kept overnight, however, it regains its ordinary properties. The direct rays of the sun are necessary for this effect, and their influence is not prevented by the use of coloured, light-absorbing flasks. According to the author the action only takes place in May and June to any extent; it has not been observed in April, August, or September. T. S. P.

Photochemical Synthesis of Carbohydrates from Carbon Monoxide and Water Vapour in the Absence of Chlorophyll; Photochemical Synthesis of Quaternary Compounds. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **150**, 1690—1693).—Synthetical processes of the type occurring in plants may in some cases be effected by the aid of the quartz-mercury lamp. The following reactions have been studied from this point of view, and carried out through the agency of ultra-violet light: $CO + O \rightleftarrows CO_2$; $CO + H_2 \rightleftarrows H{\cdot}CHO$; $xCH_2O \rightleftarrows (CH_2O)_x$; $H_2 + O \rightleftarrows H_2O$. Formamide has been obtained by exposing a mixture of carbon monoxide and ammonia to ultra-violet light. W. O. W.

Carnine and Inosic Acid. IV. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1910, **31**, 357—361. Compare Abstr., 1909, i, 322, 540).—The pentose obtained from inosine and inosic acid has been regarded previously by the authors as *d*-lyxose, mainly on account of the m. p. of the phenylbenzylhydrazone. They have now prepared lyxose from galactonic acid by means of mercuric oxide by Guerbet's method, and find that its phenylbenzylhydrazone depresses the m. p. of that of the pentose 40°. The pentose, therefore, has been converted into the *p*-bromophenylhydrazone; this has m. p. 166°, corresponding with that of *l*-ribose-*p*-bromophenylhydrazone. The authors agree, therefore, with Levene that the pentose from inosine is *d*-ribose.

C. S.

Identity of Crystallised Aloinose with *d*-Arabinose. EUGÈNE LÉGER (*Compt. rend.*, 1910, **150**, 1695—1697. Compare this vol., i, 463).—Aloinose is shown to be identical with *d*-arabinose. Inasmuch as barbaloin and *iso*barbaloin yield the same products on hydrolysis, they would appear to be stereoisomeric glucosides. W. O. W.

isoMaltol. ARNOLD BACKE (*Compt. rend.*, 1910, **151**, 78—80).—The name *isomaltol* is suggested for the compound the preparation of which from bread or biscuits has already been described (this vol., i, 225). It is very stable, and forms crystals having the composition $C_6H_6O_3$; m. p. 98°. It forms a yellow solution in aqueous sodium carbonate, liberating carbon dioxide. The compound reduces Fehling's solution, and gives the iodoform reaction; the *benzoyl* derivative has m. p. 99°. The crystalline *copper* salt, $Cu(C_6H_5O_3)_2,H_2O$, is much more stable than the corresponding salt of maltol. The *methyl* derivative, obtained by the action of diazomethane, crystallises in tablets, m. p. 102°, subliming in long needles. *iso*Maltol also differs from maltol in not yielding acetic acid on hydrolysis, and in the formation of a yellow, crystalline *compound*, m. p. 138°, when treated with amyl nitrite. Phenylhydrazine brings about decomposition. The following constitution is suggested for *iso*maltol: $OH\cdot C{<}^{CH——O}_{CO\cdot CMe}{>}CH$.

W. O. W.

Properties of Lintner's Soluble Starch. E. D. CLARK (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, **7**, lv—lvii).—The result of dialysing solutions of soluble starch, precipitating the solution left in the dialyser by means of alcohol and a drop of 10% sodium chloride solution, and examining both the precipitate and the solution leads the author to the conclusion that soluble starch carries associated with it certain amounts of dextrins with reducing properties, and that it can only be partially freed from these by dialysis or precipitation.

Soluble starch of low reducing power can be prepared in a few minutes by the following process: A thick starch paste made by pouring a suspension of 4 grams of potato starch in 15 c.c. of cold water into 200 c.c. of water at 95°, is cooled to 40°, and then mixed with 5 c.c. of filtered saliva and stirred rapidly. In two or three minutes the whole is liquefied, and is then poured into 95% alcohol and a drop of 10% sodium chloride solution added. The soluble starch is filtered quickly, dropped into a little boiling water to destroy ptyalin, and immediately cooled. The substance is readily soluble in water, whereas Lintner's starch is not.

J. J. S.

Autoxidation of Ethyl Dialkylthiocarbamates. OTTO BILLETER (*Ber.*, 1910, **43**, 1853—1857. Compare Delepine, this vol., i, 295).—Ethyl dimethylthiocarbamate and analogous esters fume and phosphoresce in contact with atmospheric oxygen, giving rise to a characteristic odour, analogous to that formed during the autoxidation of phosphorus. In closed vessels the phenomenon ceases after a short time, and is also inhibited by pressures of 5—10 atmospheres. The action is most pronounced in the presence of alkalis, and neither ozone nor hydrogen peroxide appears to be formed. In open vessels and under favourable conditions, the process continues until all the substance is used up.

The velocity of the absorption of oxygen remains constant until nearly the end of the operation, provided the pressure of the oxygen

is constant and that regular shaking is adopted. Toward the end the rate diminishes rapidly, then increases again, and becomes constant, but with a velocity some 1/100th of the original.

It is probable that the thiocarbamate first forms an unstable peroxide, which decomposes, yielding the carbamate, $NMe_2\cdot CO\cdot OEt$, and sulphur monoxide, and that the latter reacts with the alkali present, forming a thiosulphate. In most cases more than the theoretical amount of oxygen is absorbed, owing to the formation of sulphite and sulphate, and salts of an acid, $H_2S_3O_5$. This acid can be regarded as a mixed anhydride of sulphurous and thiosulphuric acid. The *sodium* salt, $Na_2S_3O_5,10H_2O$, forms definite crystals, and is oxidised by iodine to sodium trithionate: $Na_2S_3O_5 + H_2O + I_2 = Na_2S_3O_6 + 2HI$. Potassium disulphide, on the other hand, converts it into thiosulphate:

$$Na_2S_3O_5 + Na_2O + K_2S_2 = 2Na_2S_2O_3 + K_2S.$$

Methyl dimethylthiocarbamate, $NMe_2\cdot CS\cdot OMe$, is a colourless liquid, b. p. 68·2°/10 mm., m. p. 3 2°, and D_4^{15} 1·0773. The *ethyl* ester has b. p. 82·6°/10 mm., m. p. 14·3°, and D_4^{15} 1·0343; the *propyl* ester, b. p. 96·5—97·5°/12 mm., and D_4^{15} 1·0160; the iso*butyl* ester, m. p. 28·8°, and the iso*amyl* ester, $NMe_2\cdot CS\cdot OC_5H_{11}$, b. p. 119—119·5°/10 mm., and D_4^{15} 0·9688.

Methyl diethylthiocarbamate, $NEt_2\cdot CS\cdot OMe$, has b. p. 105·2—105·6°/10 mm., and D_4^{15} 1·0078.

Other sulphur compounds, such as ethyl carbamate, ethyl phenylethylcarbamate, ethyl thiocarbonate, and tetramethylcarbamide, do not appear to be capable of absorbing oxygen.

Tetramethylthiocarbamide, $CS(NMe_2)_2$, forms colourless crystals, m. p. 73·8°. J. J. S.

New Case of Spontaneous Oxidation with Phosphorescence. MARCEL DELÉPINE (*Compt. rend.*, 1910, **150**, 1607—1608. Compare this vol., i, 295).—The property of spontaneous phosphorescence exhibited by compounds containing the $S\colon\dot{C}\cdot O\cdot$ group is shared by thiocarbonyl chloride. Substances containing the $O\cdot CS\cdot NH_2$ group, or the $\cdot S\cdot\dot{C}\colon O$ or $\cdot S\cdot\ddot{C}\cdot O\cdot$ groupings, are not phosphorescent. W. O. W.

Crystallography of the Salts of Methylguanidine. ARTHUR SCHWANTKE (*Arch. Pharm.*, 1910, **248**, 390—397).—The crystallographic examination of the platinichloride and the aurichloride of the methylguanidine obtained by Schenck by the oxidation of γ-methylglycocyamidine (this vol., i, 546) proves the identity of these salts with the corresponding salts of the methylguanidine obtained by the oxidation of creatine or from methylamine and cyanamide. C. S.

Synthetical Homocholines. FERNAND MALENGREAU and A. LEBAILLY (*Zeitsch. physiol. Chem.*, 1910, **67**, 35—41).—Several homocholines have been synthesised in order to compare them with neosine, which is also a homologue of choline, according to Kutscher and Ackermann (Abstr., 1908, i, 675).

γ-*Homocholine* (γ-*hydroxytrimethylpropylammonium chloride*),

$$OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_3Cl,$$

obtained by heating trimethylenechlorohydrin with a 33% trimethylamine solution at 100° for six hours, forms large, colourless, prismatic crystals, which are deliquescent. The *hydroxide* forms a syrup, which slowly crystallises. The *aurichloride*, $C_6H_{16}ONAuCl_4$, forms glistening plates, m. p. 183° (corr.), and the *platinichloride*, $(C_6H_{16}ON)_2PtCl_6$, crystallises from 85% alcohol in characteristic, long, silky, orange-red needles, m. p. 227—228° (corr.). These salts are quite different from those of a γ-homocholine described by Schmidt and Partheil (Abstr., 1892, 950).

β-Hydroxytrimethylpropylammonium chloride (*β-homocholine*), $OH\cdot CHMe\cdot CH_2\cdot NMe_3Cl$, obtained by heating propylene chlorohydrin, $CH_2Cl\cdot CHMe\cdot OH$, with 33% alcoholic trimethylamine solution at 100° for six hours, forms extremely deliquescent crystals. The *hydroxide* is a syrup, and at 170—180° yields trimethylamine and the glycol. The *aurichloride*, $C_6H_{16}ONAuCl_4$, crystallises in glistening, golden-yellow plates, m. p. 195—196° (corr.). The *platinichloride*, $(C_6H_{16}ON)_2PtCl_6$, crystallises in orange-yellow, regular octahedra. The two isomeric bases are most readily distinguished by means of their characteristic platinichlorides.

An isomeric β-homocholine (*iso*propyleneneurine),

$$OH\cdot CH_2\cdot CHMe\cdot NMe_3Cl,$$

has been described by Morley (Abstr., 1881, 151). J. J. S.

Glycocyamine and Glycocyamidine. MARTIN SCHENCK (*Arch. Pharm.*, 1910, **248**, 376—389).—The derivative obtained by the methylation of glycocyamidine, and regarded as δ-methylglycocyamidine by Korndörfer (Abstr., 1905, i, 29), is proved by oxidation by alkaline 5% potassium permanganate at 50—60° to be γ-methylglycocyamidine, $NH:C<\begin{matrix} NH-CH_2 \\ NMe\cdot CO \end{matrix}$, since the products are oxalic acid and the same methylguanidine as is obtained by the oxidation of creatinine. A comparative experiment on the oxidation of creatinine by the preceding oxidising mixture shows that, not only methylguanidine, but also guanidine itself is formed. C. S.

Compounds of Amino-acids and Ammonia. VI. PETER BERGELL and THEODOR BRUGSCH (*Zeitsch. physiol. Chem.*, 1910, **67**, 97—103. Compare Bergell and Wülfing, this vol., i, 304).—*dl*-Leucinamide is fermented by liver extract, and yields *d*-leucinamide; the same type of reaction is brought about by kidney extract.

dl-Alanimide also undergoes asymmetric fermentation to a certain extent when left in contact with kidney extract or meat extract.

Löb and Higuchi's placenta powder is without action on leucinamide, whereas placenta magma ferments both leucinamide and alanimide, and yields the active compounds.

dl-Leucinamide gives an onion-red coloration with dilute sodium hydroxide and a drop of very dilute copper sulphate solution; the addition of more copper sulphate produces a violet-red coloration, and with concentrated solutions a heavy precipitate is formed. When dissolved in dilute hydrochloric acid, neutralised with *N*-sodium

hydroxide, filtered, and evaporated under reduced pressure, flat, onion-red prisms are obtained; they melt at 222—223° (corr., decomp.), and contain C 29·69, H 8·14, N 17·25, and Cu 19·7%. J. J. S.

Diazoaminotetrazolic Acid. KARL A. HOFMANN and HEINRICH HOCK (*Ber.*, 1910, **43**, 1866—1871. Compare this vol., i, 232, 446).—Sodium nitrite in the presence of acetic acid reacts in the cold with aminoguanidine dinitrate, yielding a *sodium* salt, $C_2H_2N_{11}Na,2H_2O$, which is regarded as the salt of *diazoaminotetrazolic acid*,

$$N_3\cdot C(:NH)\cdot N:N\cdot NH\cdot C(:NH)\cdot N_3.$$

The acid crystallises in doubly refracting, glistening lamellæ containing $1H_2O$ after drying under reduced pressure over phosphoric oxide. It is a strong tribasic acid.

The *disodium* salt, $C_2HN_{11}Na_2,H_2O$, crystallises in orange-red prisms, and yields yellow aqueous solutions which are slightly acid. The *barium* salt, $(C_2N_{11})_2Ba_3 8H_2O$, forms sulphur-yellow plates, which rapidly effloresce. The *ammonio-copper* salt, $(C_2N_{11})_2Cu_3,2NH_3$, crystallises in dark green, pleochroic plates; when mixed with potassium chlorate and gum, it forms a powerful detonator. The acid and all the salts explode when heated.

The *disilver* salt, $C_2HN_{11}Ag,H_2O$, is obtained by washing the precipitated salt with dilute ammonia and then with dilute nitric acid; if the washing with nitric acid is omitted, the *tertiary silver* salt, $C_2N_{11}Ag_3$, is obtained.

The acid and its salts are stable towards nitrous acid, but are decomposed by stannous chloride and hydrochloric acid, yielding aminotetrazole and tetrazylhydrazine (Thiele and Marais, Abstr., 1893, i, 441): $HN_4C\cdot N:N\cdot NH\cdot CN_4H + 4H = HN_4C\cdot NH\cdot NH_2 + NH_2\cdot CN_4H$.

This supports the constitution ascribed to the acid, and further confirmation is obtained by the synthesis of the acid by partial diazotisation of aminotetrazolic acid.

When boiled with acidified water, the sodium salt yields nitrogen and cyanogen, together with aminotetrazole, a decomposition analogous to that of diazoaminotetrazole to aminotetrazole, nitrogen, and cyanogen. With permanganate and dilute sulphuric acid, more than seven atoms of oxygen are taken up by the acid. J. J. S.

Alkyl Derivatives of Sodium and Their Reactions with Ethers. PAUL SCHORIGIN (*Ber.*, 1910, **43**, 1931—1938. Compare Abstr., 1907, i, 753; 1908, i, 867, 881).—The reaction between sodium and mercury diethyl takes place in the following stages at 100—170°: $Hg(C_2H_5)_2 + 2Na = Hg + 2C_2H_5Na$, $2C_2H_5Na + 2Hg = 2NaHg + C_2H_4 + C_2H_6$ (compare Buckton, *Annalen*, 1859, **112**, 220), as equal volumes of ethylene and ethane are formed during the reaction. Butane is not formed (compare Krafft and Göttig, *Ber.*, 1888, **21**, 3180). When sodium reacts with mercury diethyl in a solution of light petroleum, ether, or hexane, black, spontaneously inflammable incrustations are formed on the surface of the sodium, and the liquid remains clear; when ether is used as solvent, a voluminous precipitate of sodium ethoxide is formed, according to the equation: $C_2H_5Na + (C_2H_5)_2O = C_2H_5ONa + C_2H_6 + C_2H_4$. It is possible that an

additive compound, OEt_3Na, is first formed, and that this subsequently decomposes. Other ethers react in a similar manner. Sodium *iso*amyl (from sodium and mercury di*iso*amyl) and ethyl ether yield sodium ethoxide and not sodium *iso*amyl oxide. Sodium ethyl and phenetole yield sodium phenoxide. J. J. S.

Secondary Action of Aluminium Chloride on Aromatic Chloro-compounds. JAMES LAVAUX and MAURICE LOMBARD (*Bull. Soc. chim.*, 1910, [iv], 7, 539—542).—Friedel and Crafts explained the formation of dimethylanthracene in the action of benzyl chloride on toluene in presence of aluminium chloride as due to the occurrence of some xylyl chloride in the benzyl chloride used, but this explanation is invalid, since if xylyl chloride yields dimethylanthracene under these conditions, benzyl chloride should yield anthracene, and further it has been shown that benzyl chloride, free from xylyl chloride, still furnishes dimethylanthracene. Re-investigation of the products formed in this type of reaction indicates that two reactions may occur, represented by the following equations: $R{\cdot}Me + AlCl_3 = R{\cdot}AlCl_2 + MeCl$ and $R{\cdot}CH_2Cl + AlCl_3 = R{\cdot}AlCl_2 + CH_2Cl_2$. The methyl chloride thus formed reacts with aromatic hydrocarbons to form polymethylbenzenes, and the methylene chloride condenses with aromatic hydrocarbons, or in their absence with the aromatic chloro-compounds, to give anthracenes, the latter being always a secondary reaction. In support of these views, the following results of condensations in presence of aluminium chloride are given. Benzyl chloride reacts (1) with benzene to furnish diphenylmethane and anthracene; (2) with toluene to give phenyltolylmethane and a mixture of 1 : 6- and 2 : 7-dimethylanthracenes. Xylyl chloride condenses with toluene to give ditolylmethane and a mixture of 1 : 6- and 2 : 7-dimethylanthracenes. Benzyl chloride alone condenses to form "benzylene resin," $(C_6H_5{\cdot}CH)_n$, which on distillation yields some anthracene. Xylyl chloride also yields "benzylene resin," but in addition small quantities of the 1 : 6- and 2 : 7-dimethylanthracenes. T. A. H.

Compounds of Trinitrobenzene with Hydrazine, Phenylhydrazine, and Azobenzene: The Side Valency of the Nitro-group. KARL A. HOFMANN and H. KIRMREUTHER (*Ber.*, 1910, 43, 1764—1767).—Trinitrobenzene forms well-characterised crystalline compounds with hydrazine, phenylhydrazine, and azobenzene, of which the two former are deep red and the third is orange in colour. These are regarded as true molecular compounds, as they are quantitatively decomposed by solvents, for example, water, into their components.

The hydrazine salts of the nitrophenols are lighter and more faintly coloured than trinitrobenzene hydrazine. Trinitro-xylene and trinitromesitylene do not form similar coloured molecular compounds with hydrazine; trinitrotoluene yields a red solution, but the compound with hydrazine could not be obtained crystalline.

Trinitrobenzene-dihydrazine, $C_6H_3(NO_2)_3,2NH_2{\cdot}NH_2$, forms crystals, m. p. 122—123° (decomp.), which are deep red by transmitted light, but have a metallic green lustre.

Trinitrobenzene-phenylhydrazine, $C_6H_3(NO_2)_3,N_2H_3Ph$, forms dark

red, long, flat prisms, which sinter at 75—80° and decompose with a slight explosion.

Ditrinitrobenzeneazobenzene, $[C_6H_3(NO_2)_3]_2$,Ph·N_2·Ph, forms orange, four-sided plates, m. p. 131—132°, to a red liquid, which explodes when superheated. E. F. A.

Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1909, 145—147).—This report deals with the nitro-derivatives of *o*-xylene, the synthesis of *iso*phorone and its homologues, and the constitution of Harries and Antoni's "1 : 1-dimethyl-$\Delta^{2,5}$-*cyclo*hexadiene." E. H.

Two Solid Polymeric Nitroso-ψ-cumenes. EUGEN BAMBERGER (*Ber.*, 1910, **43**, 1842—1849. Compare Cain, Trans., 1908, **93**, 683).—ψ-Cumidine, when oxidised at 0° to 5° with a neutral solution of Caro's reagent, yields a mixture of two solid *nitroso-ψ-cumenes* (5-*nitroso*-1 : 2 : 4-*trimethylbenzene*, NO·$C_6H_2Me_3$). The crude product is purified by treatment with cold very dilute hydrochloric acid, and then by steam distillation. The colourless crystals are obtained when the hot alcoholic solution is rubbed with a glass rod. If the solution is left without stirring or rubbing, green crystals, mixed with a few colourless crystals, m. p. 65°, are obtained. The green compound is metastable, and passes more or less readily into the colourless. The green compound can also be prepared by melting the colourless form and cooling the melt rapidly by means of cold water. It has a bluish-green colour, melts at 45—46°, and is much more readily soluble than the colourless modification in most organic solvents.

Other nitroso-derivatives which form green crystals appear to exist in the one form only. The author has not succeeded in preparing Cain's colourless *p*-nitrosoacetanilide (*loc. cit.*). The green form has m. p. 179·5—180·5° (corr.).

ψ-Cumylhydroxylamine, $C_6H_2Me_3$·NH·OH, crystallises in glistening, colourless, flat needles, m. p. 103·5—104°, and yields 1 : 2 : 5-trimethylquinol when left in contact with dilute sulphuric acid for several days (compare Abstr., 1903, i, 557). J. J. S.

Isomorphous Sulphonic Derivatives of Benzene. HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WYNNE (*Brit. Assoc. Report*, 1909, 141—143).—This report deals with the crystallographic relationships of *p*-dibromobenzene-sulphonyl chloride and bromide, -sulphonanilide, and ethyl sulphonate, 1-chloro-4-iodobenzene-3-sulphonyl chloride and bromide, and *p*-di-iodobenzene-sulphonyl chloride towards each other and towards benzene, with especial reference to the Pope-Barlow theory. E. H.

Reaction between Organic Magnesium Compounds and Dibromoanthracene Tetrabromide. WLADIMIR NAUMOFF (*J. pr. Chem.*, 1910, [ii], **82**, 181—182).—Magnesium phenyl, tolyl, mesityl and ethyl bromides react with dibromoanthracene tetrabromide in ethereal solution with the formation of dibromoanthracene, simply withdrawing four atoms of bromine. T. S. P.

9 : 9-Dichlorofluorene and its Conversion into Bidiphenylene-ethene. JULIUS SCHMIDT and HANS WAGNER (*Ber.*, 1910, 43, 1796—1802).—Fluorenone, when heated with phosphorus pentachloride, is converted into 9 : 9-*dichlorofluorene*, the colour change from glistening yellow, $>CO$, to the colourless, $>CCl_2$, group being very marked. The chlorine can be eliminated from this compound by means of copper powder, forming first dichloro-*s*-bidiphenylene-ethylene, which is colourless, and then bidiphenylene-ethylene,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>C:C<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$$

(compare Graebe, Abstr., 1896, i, 566), which is intense red. It is conveniently prepared by this reaction. 9 : 9-Dichlorofluorene reacts with phenylhydrazine, hydroxylamine, etc., similarly to fluorene, and gives the same products, but more readily.

Dichlorofluorene forms colourless quadrants, m. p. 99°, and dissolves in concentrated sulphuric acid with a violet coloration.

Dichloro-*s*-bidiphenylene-ethane, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>CCl\cdot CCl<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, separates in colourless crystals, m. p. 230—232°.

Fluorenone-p-*nitrophenylhydrazone*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>C:N\cdot NH\cdot C_6H_4\cdot NO_2$, prepared either from fluorenone or from dichlorofluorene, crystallises in orange-yellow needles, m. p. 269°. E. F. A.

Compounds which cause the Red Coloration of Aniline. I. Effect of Oxygen and Ozone, and the Influence of Light in the Presence of Oxygen. HARRY D. GIBBS (*Philippine J. Sci.*, 1910, 5, 9—16).—Bottles containing aniline are placed in sunlight and constantly agitated for about one month. The stoppers are removed from time to time, and the air over the liquid changed. The deep red liquid is then dissolved in very dilute sulphuric acid; the insoluble portion contains 2 : 5-dianilinoquinone. Without being filtered, the sulphuric acid solution is extracted with ether. The ethereal extract contains dianilinoquinone, dianilinoquinoneanil, and azobenzene. Another portion of the coloured aniline is poured into 50% acetic acid; when cold, the solution deposits the characteristic twinned crystals of azophenine.

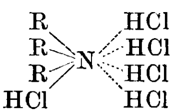
Dry purified aniline, free from sulphur compounds, can be kept unchanged for two months in an atmosphere of an inert gas. In dry, purified oxygen, the coloration of the aniline proceeds slowly in darkness and very rapidly in sunlight. The presence of moisture or impurities is not necessary for the production of the colour. In contact with ozonised oxygen, aniline is instantly coloured, rapidly becomes dark red, and evolves carbon dioxide; ultimately the liquid sets to a crystalline mass of dianilinoquinoneanil. C. S.

Addition of Hydrogen Chloride to Substituted Anilines at Low Temperatures. ANTONI VON KORCZYŃSKI (*Ber.*, 1910, 43, 1820—1824. Compare Abstr., 1909, i, 123; Kaufler and Kunz, *ibid.*, 136, 556).—The following compounds have been isolated at

$-75°$: With 8HCl, *p*-nitrosodimethylaniline; with 6HCl, *p*-nitrosoaniline; with 5HCl, *m*-nitrodimethylaniline; with 4HCl, 2 : 4-dinitroaniline, 3 : 5-dinitroaniline, 4 : 6-dibromo-2-nitroaniline; with $3\frac{1}{2}$HCl, 2 : 6-dinitroaniline; with 3HCl, aniline, diphenylamine, 4 : 6-dichloro-2-nitroaniline, 2 : 6-dichloro-4-nitroaniline, 2 : 6-dibromo-4-nitroaniline, *p*-nitrodimethylaniline, *o*-, *m*-, *p*-aminobenzoic acids; with $2\frac{1}{2}$HCl, 2 : 4-dichloroaniline, dibromo-*o*-toluidine, trichloroaniline; with 2HCl, *p*-toluidine, *o*-, *m*-, *p*-chloroanilines, *o*-, *m*-, *p*-bromoanilines, *p*-iodoaniline, 3 : 5-dichloroaniline, 3 : 5-dibromoaniline, dibromo-*p*-toluidine, 3 : 5-dichloro-2 : 4 : 6-tribromoaniline, 4-bromo-2 : 6-dinitroaniline, carbamide, thiocarbamide; with 1HCl, 6-bromo-2 : 4-dinitroaniline.

Trinitroaniline does not combine with hydrogen chloride.

The maximum number of molecules of hydrogen chloride is 5, except in the case of the nitroso-derivatives, where the oxygen atom also probably adds on hydrogen chloride. This points to the co-ordinate number 8, and the annexed type of formula is suggested.



It is noticed that monohalogen derivatives of aniline add on 2HCl, and that the introduction of a second halogen atom into the ortho- or para-position can increase the additive capacity of the amine. The introduction of 3 or even 5 halogen atoms does not prevent the formation of hydrochlorides. The introduction of a second nitro-group into the molecule of nitroaniline has much the same effect as the introduction of a second halogen atom into a monohalogen derivative of aniline. Two nitro-groups in the ortho-position with respect to the amino-group are not so favourable to addition as the same groups when in 2 : 4- or 3 : 5-positions, and the presence of three nitro-groups can prevent the formation of an additive compound.

The acid sulphate of a base as a rule combines with two molecules of hydrogen chloride less than the base itself; thus *p*-nitrosodimethylaniline sulphate forms the colourless *compound*,

$$NO\cdot C_6H_4\cdot NMe_2,H_2SO_4,6HCl.$$

Naphthaquinoline forms a compound with 5HCl, and its acid sulphate a compound with 3HCl. Quinoline acid sulphate also combines with 3HCl. Ammonium chloride, ammonium sulphate, and hydrazine sulphate do not combine with hydrogen chloride.

Most of the compounds mentioned are colourless, a few have a pale yellow colour, and the compound from nitrosoaniline is yellow.

J. J. S.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Report*, 1909, 147—149).—This report [with W. C. EVANS and W. J. JONES] deals with the transformation of *p*-chloroacetylchloroaminobenzene into dichloroacetanilide.

E. H.

Some New Thorium Salts. GEORGES KARL (*Ber.*, 1910, **43**, 2068—2070).—*Thorium picrate*, $Th(C_6H_2N_2O_7)_4,10H_2O$, separates as

an oil, which solidifies to a yellow, hard, crystalline mass, when ammonium picrate is added to a hot aqueous solution of thorium nitrate. Small, yellow needles, m. p. 52—53°; explodes on heating with the bare flame. It can be dehydrated at 105°, and then forms a vitreous, yellow mass, which is still solid at 100°. At 25°, 100 c.c. of water dissolve 0·3052 gram of the hydrated picrate.

Thorium hippurate, $(COPh \cdot NH \cdot CH_2 \cdot CO_2)_4Th$, is formed from thorium nitrate and ammonium hippurate. White, crystalline powder, slightly soluble in water. One hundred c.c. of water dissolve 0·0318 gram at 25°.

Basic thorium chloroacetates are obtained when freshly-prepared basic thorium carbonate is added to the various chloroacetic acids. *Basic thorium monochloroacetate*, $(CH_2Cl \cdot CO_2)_2Th(OH)_2,H_2O$; small, white needles from alcohol. *Basic thorium dichloroacetate*,

$$(CHCl_2 \cdot CO_2)_2Th(OH)_2;$$

small prisms from alcohol. *Basic thorium trichloroacetate*,

$$(CCl_3 \cdot CO_2)_2Th(OH)_2;$$

small, shining, and transparent octahedra, which contain water of crystallisation, but effloresce on exposure to the air. T. S. P.

Behaviour of 3-Nitro-*p*-cresol towards Sulphuric Acid. II. GUSTAV SCHULTZ and OSKAR LOW (*Ber.*, 1910, **43**, 1899—1902. Compare Abstr., 1909, i, 222).—When 3-nitro-*p*-cresol is added slowly to concentrated sulphuric acid on the water-bath, the product is the same as that obtained by the action of cold fuming sulphuric acid, namely, β-acetylacrylic acid. By-products of the reaction are a *substance* (α-nitro-β-acetylacrylic acid?), m. p. 206—207° (decomp.), and *ammonium 3-nitro-*p*-cresol-5-sulphonate*, which is reduced by stannous chloride and hydrochloric acid to the corresponding *amino*-compound.

C. S.

Action of Nitroso-derivatives on Unsaturated Compounds. ANGELO ANGELI, LUIGI ALESSANDRI, and RAFFAELLO PEGNA (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 650—659).—The authors have investigated the action of nitrosobenzene on anethole, *iso*safrole, safrole, and ethyleugenol. In the first two cases no definite reaction-product was isolated. When a mixture of safrole and nitrosobenzene is kept in the dark for four or five days at the ordinary temperature, a *substance*, crystallising in golden-yellow needles, m. p. 193°, is obtained, in addition to azoxybenzene. The compound has the formula $C_{16}H_{13}O_3N$, and the authors ascribe to it the constitution

$$CH_2O_2{:}C_6H_3 \cdot CH{:}CH \cdot CH{:}NOPh.$$

It yields nitrosobenzene when exposed to light, or to the action of oxidising agents, and, when it is oxidised with potassium permanganate in alkaline solution, piperic acid is formed. By the action of dilute mineral acids, it is converted into an isomeric *compound*, which has m. p. 195°, and the authors regard it as a Schiff's base; it is a yellow powder, is soluble in alkalis, and yields a *sulphate*, m. p. 174°. It forms a benzoyl derivative, $C_{20}H_{15}O_3N$, m. p. 229°, identical with that obtained by the action of benzoyl chloride on *p*-aminophenol. The base is also acted on readily by hydroxylamine, three oximes of the

formula $C_{10}H_9O_3N$ being produced. The *a-oxime* crystallises in long, thin needles, m. p. 195°; the *β-oxime* forms lustrous laminæ, m. p. 191°, and the *γ-oxime*, short needles, m. p. 155°. With benzoyl chloride both the *β*- and *γ*-oxime yield the same *benzoyl* derivative, $C_{17}H_{13}O_4N$, m. p. 175°. All three compounds show the behaviour of oximes. When they are boiled with dilute acid, piperonylacraldehyde is formed; this substance is, however, best prepared by the action of amyl nitrite. Whether prepared in this way or from piperonal by the method of Ladenburg and Scholtz, it has m. p. 84°, although these authors gave (Abstr., 1895, i, 42) m. p. 70°. Phenylhydroxylamine reacts with the aldehyde, forming the same compound of m. p. 193° as is obtained from safrole and nitrosobenzene.

The action of nitrosobenzene on ethyleugenol is similar to its action on safrole: a *compound*, $C_{18}H_{19}O_3N$, is formed, which crystallises in small, yellow needles, m. p. 155°. R. V. S.

Phenanthrene Series. XXVIII. Bromination and Nitration of 9-Hydroxyphenanthrene. Julius Schmidt and Otto Spoun (*Ber.*, 1910, **43**, 1802—1807. Compare Abstr., 1909, i, 134; this vol., i, 312).—By the action of bromine in carbon disulphide solution, 9-hydroxyphenanthrene yields a dibromo-derivative containing one bromine atom in position 3 in the nucleus, since it yields 3-bromophenanthraquinone on oxidation with chromic acid. The other bromine atom is in position 9 or 10, and the compound has the formula $\begin{array}{l} C_6H_3Br\cdot C(OH) \\ | \qquad\quad \| \\ C_6H_4\text{——}CBr \end{array}$ or $\begin{array}{l} C_6H_3Br\cdot CBr \\ | \qquad\quad \| \\ C_6H_4\text{——}C(OH) \end{array}$. The same compound is obtained on brominating 9-acetoxyphenanthrene, and this method is preferable.

Before nitration of 9-hydroxyphenanthrene, the hydroxyl group has to be protected by acetylation, and certain further precautions must be observed to prevent oxidation. A dinitroacetoxy-compound is obtained containing one nitro-group in position 3, and the other is either 9 or 10; it yields 3-nitrophenanthraquinone on oxidation.

3 : 9-*Dibromo*-10-*hydroxyphenanthrene* has m. p. 135°; 9-*acetoxyphenanthrene* has m. p. 77°; 3 : 9-*dibromo*-10-*acetoxyphenanthrene*, prepared by acetylation of the dibromo-derivative, crystallises in colourless needles, m. p. 177°.

3 : 9-*Dinitro*-10-*acetoxyphenanthrene* is a yellow powder, m. p. 137—138°. E. F. A.

Behaviour of Aromatic Disulphides at High Temperatures. Oscar Hinsberg (*Ber.*, 1910, **43**, 1874—1879).—When the simple aromatic disulphides are heated in a sealed tube at 240—280° they decompose into a mixture of the monosulphide and trisulphide. With more complex disulphides, other disturbing reactions take place, which may completely suppress the simple wandering of the sulphur atom.

Phenyl disulphide at 280° gives a mixture of monosulphide and trisulphide in the proportions required by the equation: $2S_2Ph_2 = SPh_2 + S_3Ph_2$. *a*-Naphthyl disulphide at 260—270° gives a mixture of the mono- and tri-sulphide. 4 : 4′-Dithioacetanilide at 180° gives a mixture of the three isomeric dithioacetanilides. At 240—260° a

mixture is obtained, from which it is difficult to separate the constituents; thus far the presence of 4 : 4′-thioacetanilide has been proved.

Dithiosalicylic acid [*o*-disulphidobenzoic acid, $S_2(C_6H_4 \cdot CO_2H)_2$] at 280° gives a mixture containing the corresponding monosulphide, 2 : 2′-dicarboxydiphenyl sulphide (this vol., i, 261), and the thioanhydride of trithiosalicylic [trisulphidobenzoic] acid, which is formed instead of the expected *o*-trisulphidobenzoic acid. The dicarboxydiphenyl sulphide also loses carbon dioxide to some extent, with the formation of phenyl-2-carboxyphenyl sulphide. o-*Trisulphidobenzoic acid thioanhydride*, $\overline{CO \cdot C_6H_4 \cdot S_3 \cdot C_6H_4 \cdot CO \cdot S}$, forms light yellow needles, m. p. 75—76°, soluble in chloroform, insoluble in sodium carbonate or cold sodium hydroxide. It slowly dissolves in warm sodium hydroxide, and the addition of hydrochloric acid to the solution precipitates o-*trisulphidobenzoic acid*, $S_3(C_6H_4 \cdot CO_2H)_2$, colourless flakes, difficultly soluble in all solvents, m. p. about 300°. In the thioanhydride, the middle ring is a 10-atom one.

Dimethyl *o*-disulphidobenzoate at 260—280° gives the dimethyl ester of 2 : 2-dicarboxydiphenyl sulphide; at the same time a wandering of the methyl group takes place with the formation of *o*-methylthiolbenzoic acid, as indicated by the scheme:

$$S_2(C_6H_4 \cdot CO_2Me)_2 \longrightarrow 2SMe \cdot C_6H_4 \cdot CO_2H.$$

T. S. P.

Basic Properties of Sulphoxides and their Tautomerism. EMIL FROMM and G. RAIZISS (*Annalen*, 1910, **374**, 90—105).—Sulphides in which the sulphur is combined with a methyl or methylene group combine with halogens, forming dihalogenides; if, however, the sulphur is united directly with aromatic groups on both sides, dihalogenides are not formed. An attempt to ascertain the behaviour towards halogens of a sulphide containing the sulphur united with a –CH group was unsuccessful; the substance investigated, namely, the *p*-tolyl mercaptal of benzaldehyde,

$$CHPh(S \cdot C_6H_4Me)_2,$$

when acted on by bromine is decomposed with the formation of tolyl disulphide.

Analogously, when a sulphoxide containing a sulphoxy-group adjacent to a methyl or methylene group is treated with hydrogen bromide, it yields a dibromide, but if the sulphoxy-group is united to two aromatic groups, as in ditolyl sulphoxide, $SO(C_6H_4Me)_2$, the sulphoxide is not attacked by hydrogen bromide.

Di-p-*tolyldithioethane*, $C_2H_4(S \cdot C_6H_4Me)_2$, is formed by the interaction of *p*-thiocresol and ethylene bromide in an alcoholic solution of sodium hydroxide; it crystallises in transparent leaflets, m. p. 80°, and when oxidised with nitric acid, chromic acid, or hydrogen peroxide yields the corresponding *disulphoxide*, $C_{16}H_{18}O_2S_2$, which crystallises in silvery, white leaflets, m. p. 166° (decomp.). The following compounds are obtained by suitable methods from the dithio-compound by treatment with chromic acid or nitric acid: p-*tolylsulphone*-p-*tolylsulphoxyethane*, $C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot SO \cdot C_6H_4Me$, long, colourless

needles, m. p. 148°; *di*-p-*tolylsulphonethane*, $C_2H_4(SO_2 \cdot C_7H_7)_2$, long, glistening, transparent crystals, m. p. 199—200°; *dinitrodi*-p-*tolylsulphonethane*, $C_{16}H_{16}O_8N_2S_2$, long, pale yellow needles, m. p. 228°; *tetranitrodi*-p-*tolylsulphonethane*, $C_{16}H_{14}O_{12}N_4S_2$, yellow leaflets, m. p. above 300°.

A solution of di-*p*-tolyldithioethane in chloroform, when treated with bromine at 0°, yields the *tetrabromide*, $C_2H_4(SBr_2 \cdot C_6H_4Me)_2$, obtained as small, glistening crystals, which appear yellowish-red by transmitted light and dark red by reflected light, m. p. 68—69°; it is so unstable that it cannot be recrystallised, and is decomposed by atmospheric moisture. The tetrabromide is converted by water at 0° into the di-*p*-tolylsulphoxyethane just described, and can be regenerated from the latter substance by treatment with hydrogen bromide. On the other hand, di-*p*-tolylsulphoxyethane is converted by bromine in chloroform into the *tetrabromide*, $C_{16}H_{18}O_2Br_4S_2$, which crystallises in red prisms, m. p. 96°.

Di-p-*tolyldithioethane di-iodide*, $C_{16}H_{18}I_2S_2$, is obtained by treating ditolyldithioethane (1 part) with iodine (1 part) in hot glacial acetic acid for a short time; it forms steel-blue needles, m. p. 83°. The *tetra-iodide*, $C_{16}H_{18}I_4S_2$, obtained by using iodine (2 parts) and heating the solution to 120° for about three hours, crystallises in wine-red leaflets, m. p. 88°.

Benzyl sulphide dibromide, $(CH_2Ph)_2SBr_2$, is obtained by acting on benzyl sulphide with a solution of bromine in chloroform at 0°, or by treating benzyl sulphoxide with hydrogen bromide; it forms yellowish-red crystals, m. p. 54°.

The p-*tolylmercaptal* of benzaldehyde, $C_{21}H_{20}S_2$, formed by the condensation of benzaldehyde and *p*-thiocresol under the influence of hydrogen chloride, crystallises in long prisms, m. p. 79°; it is oxidised by potassium permanganate, yielding *di*-p-*tolylsulphonephenylmethane*, $C_{21}H_{20}O_4S_2$, which forms stout, pointed plates, m. p. 163°.

The p-*tolylmercaptal* of acetone, $C_{17}H_{20}S_2$, is similarly prepared; it forms needles, m. p. 66°. W. H. G.

Active Pinonic and Pinic Acids. PHILIPPE BARBIER and VICTOR GRIGNARD (*Bull. Soc. chim.*, 1910, [iv], 7, 548—557).—A detailed account of work already published (Abstr., 1908, i, 852), showing that Tiemann's *l*-pinonic acid (Abstr., 1896, i, 308) is not identical with the true *l*-pinonic acid derived from *l*-pinene. It is pointed out further that the *iso*propylheptanonolide derived from Tiemann's acid is not identical with that obtained from true *l*-pinonic acid, and since the structure of the *iso*propylheptanonolide does not permit of *cis-trans*-isomerism, it follows that Tiemann's acid cannot be a *cis-trans*-isomeride of true *l*-pinonic acid. It is suggested that Tiemann's acid should be called campholonic acid, and that the acid obtained by the same author by the oxidation of β-campholenic acid should be named β-campholonic acid.

l-Pinonic acid, crystallised from water over sulphuric acid, forms large, monoclinic prisms [$a:b:c = 0{\cdot}5782:1:0{\cdot}6216$; $\beta = 105°$]. On treatment with sulphuric acid, it yields 1-iso*propylheptanonolide*,

$COMe\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}CMe_2\cdot O \\ CH_2-CO\end{matrix}$, m. p. 47—48°, $[\alpha]_D$ − 57·45° in alcohol, which separates in colourless, slender needles by addition of light petroleum to its solution in ether. On oxidation with sodium hypochlorite, *l*-pinonic acid furnished *d*-pinic acid, $[\alpha]_D$ +70·10°, and a second substance, which decomposes on distillation and may be a mixture of *cis*- and *trans*-isomerides. *d*-Pinonic acid, obtained by oxidising *d*-pinene from myrtle oil, furnishes *d*-iso*propylheptanonolide*, m. p. 47°, $[\alpha]_D$ +57·88°, and on oxidation *l*-pinic acid, m. p. 135°, which crystallises in small needles. A fused mixture of equal quantities of the two pinic acids gives *r*-pinic acid, m. p. 101—102°. In the preparation of both *l*- and *d*-pinonic acids some *r*-pinonic acid is also formed. T. A. H.

New Synthesis of Aromatic Carboxylic Acids from Hydrocarbons. II. PAUL SCHORIGIN (*Ber.*, 1910, **43**, 1938—1942. Compare Abstr., 1908, i, 886).—An examination of the gaseous products formed by the action of dry carbon dioxide on a mixture of benzene, sodium wire, and mercury diethyl proves that the reaction proceeds in the stages: (1) $HgEt_2 + 2Na = Hg + 2NaEt$; (2) $C_6H_6 + C_2H_5Na = C_6H_5Na + C_2H_6$, and (3) $C_6H_5Na + CO_2 = C_6H_5\cdot CO_2Na$, as the proportion of ethane to ethylene is much greater (12 : 1) than is obtained by the action of sodium on mercury diethyl (this vol., i, 547). Benzoic acid can also be obtained by substituting sodium *iso*amyl for sodium ethyl, but the yield is not good.

The following acids have been synthesised by the action of carbon dioxide on sodium, mercury diethyl, and the respective hydrocarbon: *o*-Tolylacetic acid and *p*-tolylacetic acid from *o*- and *p*-xylenes, 3 : 5-dimethylphenylacetic acid from mesitylene, diphenylacetic acid from diphenylmethane, and *p*-homocouminic acid from *p*-cymene. The yield is poor in each case.

Thiophen-α-carboxylic acid is formed from thiophen, and the yield is somewhat better, 7 grams from 50 grams of thiophen. J. J. S.

Action of Pyridine on 2-Chloro-3 : 5-dinitrobenzoic Acid. THEODOR ZINCKE (*J. pr. Chem.*, 1910, [ii], **82**, 17—23. Compare this vol., i, 585).—When a mixture of pyridine and 2-chloro-3 : 5-dinitrobenzoic acid is kept for some hours, and is then heated for a short time on the water-bath, the *betaine*, $\begin{matrix}C_6H_2(NO_2)_2\cdot CO \\ | \qquad\qquad | \\ C_5NH_5 \text{———} O\end{matrix}$, m. p. 186—188° (decomp.), is formed. It separates from water in colourless, rhombic plates, yields 3 : 5-*dinitro-2-anilinobenzoic acid*, m. p. 214°, or the corresponding *toluidino*-derivative, m. p. 228°, by heating with aniline or *p*-toluidine in glacial acetic acid, and the *methyl* ester, m. p. 128°, or the *ethyl* ester, m. p. 97°, of dinitrosalicylic acid by treatment with methyl or ethyl alcohol at 100°. The action of 2*N*-sodium hydroxide on an aqueous solution of the betaine, which is subsequently acidified, leads to the formation of a reddish-brown, crystalline *substance*, $C_{12}H_9O_7N_3,H_2O$, m. p. 135—140° (decomp.), which regenerates the betaine by heating with hydrogen chloride in glacial acetic acid, yields

3 : 5-dinitro-2-aminobenzoic acid by treatment with boiling glacial acid and concentrated hydrochloric acids, and forms the dianilide, $NPh:CH\cdot CH:CH\cdot CH:CH\cdot NHPh$ (Abstr., 1904, i, 921), and dinitroaminobenzoic acid when boiled with an excess of aniline and a little alcohol. The substance is, therefore,

$$CO_2H\cdot C_6H_2(NO_2)_2\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot OH$$

or $CO_2H\cdot C_6H_2(NO_2)_2\cdot N:CH\cdot CH:CH\cdot CH_2\cdot CHO$. C. S.

Lactonoid Anhydrides of Acylated Amino-acids. IV. Behaviour of Hippuric Acid, Hippuramide, and *r*-Acetylalanine towards Dehydrating Agents. ERNST MOHR and FR. STROSCHEIN (*J. pr. Chem.*, 1910, [ii], **82**, 60—64).—A continuation of the preceding paper (this vol., i, 483). Attempts to prepare the lactonoid anhydride of hippuric acid by heating the acid with acetic anhydride have been unsuccessful, as also have been experiments on the formation of a cyclic imide by heating hippuramide with *N*-sodium hydroxide or with acetic anhydride. Also, the heating of *r*-acetylalanine and acetic anhydride does not yield a product from which the lactone can be isolated. C. S.

General Reaction for the Conversion of Saturated Fatty Acids, $CH_2R\cdot CH_2\cdot CO_2H$, into Ketones, $R\cdot CO\cdot CH_3$. HENRY D. DAKIN (*Amer. Chem. J.*, 1910, **44**, 41—48).—The generality of the reaction whereby the sodium or ammonium salts of fatty acids are converted into ketones to the extent of 5—10% by excess of 3% hydrogen peroxide (Abstr., 1908, i, 74, 119 ; ii, 720) has been tested. In addition to the cases already recorded, it is found that phenylacetic acid yields benzaldehyde, and phenylbutyric acid a volatile ketone with the odour of benzyl methyl ketone. C. S.

New Method of Alkylation with Benzyl Cyanide. Alkylation of Nitriles of the Formula $CHPhR\cdot CN$. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1910, [iv], **7**, 666—670, 670—672).—An extended account of work already dealt with (this vol., i, 257, 482), fuller details of the method of working being given. The following new data are recorded.

a-Phenyl-β-methylbutyric acid, m. p. 61—62°, obtained by boiling the corresponding nitrile (*loc. cit.*) during thirty-six hours with potassium hydroxide in alcohol, or during six hours if amyl alcohol is used as a solvent, crystallises in colourless prisms.

a-Phenyl-a-ethylbutyramide, m. p. 52°, obtained by hydrolysis of the nitrile (*loc. cit.*), forms colourless prisms, as does also *a-phenyl-γ-methyl-a-propylvaleramide*, $CHMe_2\cdot CH_2\cdot CHPr^a Ph\cdot CO\cdot NH_2$, m. p. 84—85°. T. A. H.

1-Acetyl-1-methyl*cyclo*hexane. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1910, **150**, 1606—1607. Compare Abstr., 1909, i, 796).—Oxidation of the ketone obtained by the action of acids on *cyclo*hexanolpropan-*β*-ol leads to the formation of the *ketonic acid*, $C_6H_{10}Me\cdot CO\cdot CO_2H$, b. p. 141°/20 mm. This forms a *semicarbazone*, m. p. 198°, and a *semicarbazone methyl* ester, m. p. 158°; the *oxime*

decomposes at 160°, losing water and carbon monoxide, and forming the *nitrile*, C_7H_{13}·CN, b. p. 180°, which, on hydrolysis, furnishes an acid identical with Zelinski's 1-methyl*cyclo*hexane-1-carboxylic acid (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 477). The original ketone, therefore, is 1-*acetyl*-1-*methyl*cyclo*hexane*, C_6H_{10}Me·COMe. W. O. W.

α-Amino-*p*-hydroxyphenylacetic Acid. JULES ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1910, [iv], 7, 516—518).—The first part of an investigation of the homologues of tyrosine, which are likely to be of biological interest. The preparation and properties of α-amino-*p*-hydroxyphenylacetic acid, the next lower homologue, are described. The acid was prepared by the action of potassium cyanide and ammonium chloride on anisaldehyde, the resulting aminonitrile being hydrolysed and the acid obtained demethylated by Zeisel's method.

α-Amino-p-*methoxyphenylacetonitrile*, OMe·C_6H_4·CH(NH_2)·CN, m. p. 65°, is unstable, and evolves hydrogen cyanide at atmospheric temperatures; the *hydrochloride* is crystalline. The corresponding acid already prepared by Tiemann and Köhler (Abstr., 1882, 57) yields a crystalline hydrochloride, and on demethylation gives *α-amino*-p-*hydroxyphenylacetic acid*, which crystallises in long, colourless prisms, and yields crystalline *salts* with halogen acids and a pale blue, crystalline *copper* derivative. Chlorine water and bromine water give precipitates; the *bromo*-compound so formed has m. p. 90°. The acid may be characterised by its copper derivative, the red colour produced by Millon's reagent, the blue tint furnished by alkaline hypochlorites, and the fact that tyrosinase produces no change in colour. The last two tests serve to distinguish this acid from tyrosine. T. A. H.

Reduction and Derivatives of *o*-Nitrocinnamoylformic Acid. GUSTAV HELLER (*Ber.*, 1910, **43**, 1923—1927).—[With EDMUND WEIDNER]—*o*-Nitrocinnamoylformic acid forms an *ethyl* ester, m p. 71°, which separates from alcohol in golden-yellow needles, an *oxime*, m. p. 157°, and *cis*- and *trans*-modifications of the *phenylhydrazide*. The *cis*-form, obtained from the acid and phenylhydrazine in alcohol at 0°, is precipitated from acetone solution by petroleum in tufts of faintly yellow needles, responds to Bülow's hydrazide reaction, easily and smoothly yields indigotin by treatment with alkaline water, and is converted at 100° or by recrystallisation from 50% acetic acid into the *trans*-isomeride, m. p. 222° (decomp.), which is produced directly by treating a hot solution of the acid in 50% acetic acid with phenylhydrazine. The *trans*-modification gives Bülow's reaction, but does not yield indigotin with alkaline water. *o*-Nitrocinnamoylformic acid in ethereal solution is reduced by aqueous ferrous sulphate and ammonium hydroxide to 4-keto-1 : 4-dihydroquinoline-2-carboxylic acid. C. S.

Complete Methylation with Methyl Sulphate. JOSEF TAMBOR (*Ber.*, 1910, **43**, 1882—1889).—Waliaschko's extension (Abstr., 1909, i, 248) of Dreker and Kostanecki's generalisation (Abstr., 1893, i, 217) has been supported by the author's experiments, which show that the following fully methylated compounds can be obtained by submitting the partially methylated substances to the repeated energetic action of

methyl sulphate and alkali. 1-Methoxyxanthone from 1-hydroxyxanthone; 2-methoxy-4-ethoxyacetophenone, m. p. 49°, from resacetophenone ethyl ether; 4-methoxy-2-ethoxyacetophenone, m. p. 7°, from resacetophenone methyl ether and ethyl sulphate; resacetophenone dimethyl ether, m. p. 44°, from the monomethyl ether; 2-hydroxy-4-methoxydeoxybenzoin, m. p. 90°, from 2 : 4-dihydroxydeoxybenzoin, and by a repetition of the precess, 2 : 4-dimethoxydeoxybenzoin, m. p. 56°.

[With A. SCHÜRCH]—*Methyl* 2′-*hydroxy*-4′-*methoxy*-2-*benzoylbenzoate*, $OMe\cdot C_6H_3(OH)\cdot CO\cdot C_6H_4\cdot CO_2Me$, m. p. 103°, and the corresponding acid are both obtained when ethyl resorcinolphthalein is heated for twelve hours with methyl iodide (2 mols.) and alcoholic potassium hydroxide (2 mols.). Ethylation of resorcinolphthalein in a similar manner yields 2′-*hydroxy*-4′-*ethoxy*-2-*benzoylbenzoic acid*, m. p. 173°, and its ethyl *ester*, m. p. 78°. Reduction of 2′-hydroxy-4′-methoxy-2-benzoylbenzoic acid by zinc dust and alcoholic potassium hydroxide leads to the formation of 2′-*hydroxy*-4′-*methoxy*-2-*benzylbenzoic acid*, m. p. 140°, a hot alcoholic solution of which with methyl sulphate (3 mols.) and potassium hydroxide (3 mols.) forms the potassium salt of 2′ : 4′-*dimethoxy*-2-*benzylbenzoic acid*, m. p. 149°; the acid in carbon disulphide is converted by phosphorus pentachloride into the corresponding acid *chloride*, m. p. 166°. Resorcinolphthalein is easily and completely methylated by methyl sulphate (3 mols.) and potassium hydroxide (3 mols.), yielding *methyl* 2′ : 4′-*dimethoxy*-2-*benzoylbenzoate*, m. p. 100°. 2′ : 4′-Dimethoxy-2-benzoylbenzoic acid is reduced by zinc dust and alkali to the 2 : 4-*dimethoxyphenylphthalide*,

$$C_6H_3(OMe)_2\cdot CH{<}^{\text{---}O\text{---}}_{C_6H_4}{>}CO,\ \text{m. p. } 107°.$$

β-Resorcylic acid, methyl sulphate, and sodium hydroxide yield, according to the experimental conditions, either *p*-methoxysalicylic acid or β-resorcylic acid dimethyl ether. The chloride of the latter and phloroglucinol trimethyl ether condense in the presence of aluminium chloride to form 2 : 4 : 6 : 2′ : 4′-*pentamethoxybenzophenone*, m. p. 138°, which is reduced by zinc and alcoholic alkali to 2 : 4 : 6 : 2′ : 4′-*pentamethoxybenzhydrol*, m. p. 104°. 2 : 4 : 2′ : 4′-*Tetramethoxybenzophenone* has m. p. 130°. 3 : 4 : 2′ : 4′-*Tetramethoxybenzophenone*, m. p. 124°, separates from concentrated alcoholic solution in yellow, prismatic needles, and from dilute solution in small, white leaflets. 2′ : 4 : 4′-*Trimethoxybenzophenone* has m. p. 73—74°. C. S.

Researches in Benzidine Formation. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 677—683).—A résumé of information already published, in part, in Abstr., 1905, i, 651; 1909, i, 747. The following new data are given. 2 : 2′-Dinitrodiphenylmethane-4 : 4′-dicarboxylic acid, when purified through the ethyl ester, has m. p. 296°, and dissolves in excess of alkali, forming a violet-coloured solution. On reduction with stannous chloride and hydrochloric acid in alcohol, the ethyl ester yields ethyl 2 : 2′-diaminodiphenylmethane-4 : 4′-dicarboxylate, m. p. 150° (compare Abstr., 1905, i, 651), whilst reduction with zinc dust and ammonium chloride, followed by oxidation by means of a current of air in presence of potassium hydroxide,

furnishes 2 : 2′-azoxydiphenylmethane-4 : 4′-dicarboxylic acid (Abstr., 1909, i, 747). The *ethyl* ester of this acid, m. p. 224°, crystallises in bright yellow needles, and on reduction with zinc dust and acetic acid yields *ethyl* 2 : 2′-*hydrazodiphenylmethane*-4 : 4′-*dicarboxylate*, m. p. 165°, which crystallises in colourless needles, and on oxidation with yellow mercuric oxide gives ethyl 2 : 2′-azodiphenylmethane-4 : 4′-dicarboxylate (*loc. cit.*). T. A. H.

Condensation of Ethyl Oxalate with *o*- and *p*-Xylylene Cyanides. WILHELM WISLICENUS and OTTO PENNDORF (*Ber.*, 1910, **43**, 1837—1842. Compare Hinsberg, this vol., i, 486).—The small yields of xylylene cyanides obtained by the action of an aqueous-alcoholic potassium cyanide solution on the bromides are due to the formation of xylylene diethyl ethers. A theoretical yield of the p-*ether*, $C_{12}H_{18}O_2$, can be obtained by the action of an alcoholic solution of potassium ethoxide on *p*-xylylene bromide. It is a colourless liquid, b. p. 251—252°/734 mm., with a pleasing odour, and when boiled with concentrated hydrochloric acid yields *p*-xylylene chloride.

An 80% yield of *o*-xylylene cyanide can be obtained if suitable precautions are taken. A benzene solution of this cyanide condenses with ethyl oxalate in the presence of sodium ethoxide, yielding Hinsberg's 2 : 3-dihydroxy-1 : 4-dicyanonaphthalene,

$$C_6H_4<\begin{matrix}C(CN):C\cdot OH\\ \vert \\ C(CN):C\cdot OH\end{matrix},$$

which crystallises in colourless needles, containing $1H_2O$, m. p. 278—279°; when anhydrous the compound has m. p. 290—291° (decomp.). With only a small amount of ferric chloride, it gives a reddish-violet coloration, but with a larger quantity of the ferric salt a deep blue colour (compare Hinsberg).

p-Xylylene cyanide also condenses with ethyl oxalate, yielding *ethyl* ωβ-*dicyano*-p-*tolylpyruvate*, $CN\cdot CH_2\cdot C_6H_4\cdot CH(CN)\cdot CO\cdot CO_2Et$, which crystallises in glistening, colourless, flat needles, m. p. 135—136°. It gives a blackish-green coloration with ferric chloride, and a brown *copper* derivative. When benzoylated in pyridine solution it yields a *benzoyl* derivative, $C_{12}H_{16}O_4N_2$, m. p. 99—101°.

With alcoholic potassium hydroxide it yields potassium oxalate and *p*-xylylene cyanide.

When boiled for ten hours with 25% sulphuric acid it yields p-*phenyleneaceticpyruvic acid*, $CO_2H\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 199—200°.

When the ester is hydrolysed by saturating with hydrogen chloride a solution in ethyl alcohol to which the theoretical amount of water has been added, a product, $C_{14}H_{13}O_5N$, m. p. 180—181°, is obtained. This is either the *imide* of p-*phenyleneacetic-oxalacetic acid*,

$$CO_2Et\cdot CH_2\cdot C_6H_4\cdot CH<\begin{matrix}CO\cdot CO\\ \vert \\ CO\cdot NH\end{matrix},$$

or *ethyl hydroxymaleinimide*-p-*phenylacetate*,

$$CO_2Et\cdot CH_2\cdot C_6H_4\cdot C<\begin{matrix}C(OH)\cdot CO\\ \vert \\ CO\text{——}NH\end{matrix}.$$

Its solutions in alkalis have a deep yellow colour, and it yields a red

sodium salt. Ethyl cyanophenylpyruvate, when hydrolysed in a similar manner, yields hydroxyphenylmaleinimide (Volhard and Henke, Abstr., 1895, i, 103). J. J. S.

Action of Light on Benzaldehyde in the Presence of Iodine. LUIGI MASCARELLI and N. BOSINELLI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 562—563).—The oil of b. p. 189—191°/18 mm., which is one of the products of this reaction, and which was formerly described (this vol., i, 389) as a dimeric form of benzaldehyde, has been further investigated, and has proved to be benzyl benzoate. It has b. p. 315—320°, is but slightly volatile in steam, and is quantitatively saponified when boiled with alcoholic potassium hydroxide.

R. V. S.

2:3-Dihydroxybenzaldehyde; *o*-Protocatechuic Aldehyde. HERMANN PAULY and KARL LOCKEMANN (*Ber.*, 1910, **43**, 1813—1814. Compare Nölting, this vol., i, 176).—2:3-*Dihydroxybenzaldehyde*, $CHO\cdot C_6H_3(OH)_2$, prepared by heating *o*-vanillin with glacial acetic acid and concentrated aqueous hydrobromic acid, crystallises in sulphur-yellow needles, m. p. 108°, and b. p. 235°. Its solution in water has a green colour, and in alkalis an orange-red colour. Its barium salt with carbonyl chloride yields the cyclic *carbonate*,

$$CHO\cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CO,$$

in the form of colourless crystals, m. p. 105°, and when this is boiled with methyl alcohol a *methyl* ester, m. p. 115°, is obtained.

The *phenylhydrazone*, m. p. 176°, and the *semicarbazone*, m. p. 226°, are colourless, whereas the Schiff's bases are intensely coloured, although the corresponding compounds derived from other dihydroxybenzaldehydes are colourless. The *anil* is bright scarlet with a bluish tinge, so also are the derivatives with β-naphthylamine and benzidine. J. J. S.

Transformation of Non-cyclic Diketones into Cyclic Compounds. EDMOND É. BLAISE and A. KOEHLER (*Bull. Soc. chim.*, 1910, [iv], **7**, 655—661).—Published already for the most part in Abstr., 1909, i, 287; and this vol., i, 463. The following additional facts are given. 2-Acetyl-1-methyl-Δ'-*cyclo*pentene, b. p. 66—68°/9 mm., or 188—189°/755 mm. (compare Perkin and Marshall, Trans., 1890, **57**, 241), yields a *semicarbazone*, m. p. 180°, and on oxidation with permanganate furnishes acetic and γ-acetyl-*n*-butyric acids. γ-Propionyl-*n*-butyric acid yields a *semicarbazone*, m. p. 196°, and a p-*nitrophenylhydrazone*, m. p. 123°, which forms microscopic crystals.

T. A. H.

Condensation of Aldehydes with Methyl Nonyl Ketone, α-Naphthyl Methyl Ketone and *p*-Methoxyacetophenone, and the Formation of Pyridine Derivatives from the Condensation Products. MAX. SCHOLTZ and W. MEYER (*Ber.*, 1910, **43**, 1861—1866. Compare Abstr., 1895, i, 563; 1899, i, 717; 1903, i, 436).—α-Benzylidenemethyl nonyl ketone [styryl nonyl ketone], $CHPh\!:\!CH\cdot CO\cdot C_9H_{19}$, has been prepared by Carette (Abstr., 1901, i, 13).

The *semicarbazone*, $C_{19}H_{29}ON_3$, crystallises in yellow needles, m. p. 121°. The isomeric γ-benzylidene derivative, obtained by condensing benzaldehyde with methyl nonyl ketone in the presence of hydrogen chloride (Goldschmidt and Krczmar, Abstr., 1902, i, 40; Harries and Müller, *ibid.*, 1902, i, 295), forms a *hydrochloride*, $C_{18}H_{27}OCl$, which crystallises in snow-white needles, m. p. 77°. The *ketone*, $CH_3\cdot CO\cdot C(:CHPh)\cdot C_8H_{17}$, is an oil, and yields a *semicarbazone*, $C_{19}H_{29}ON_3$, in the form of glistening plates, m. p. 130°.

α-Cinnamylidenemethyl nonyl ketone, $CHPh:CH\cdot CH:CH\cdot CO\cdot C_9H_{19}$, crystallises in glistening, yellow plates, m. p. 83°. The *semicarbazone*, $C_{21}H_{31}ON_3$, forms pale yellow needles, m. p. 154°, and the *oxime*, $C_{20}H_{29}ON$, yellow, felted needles, m. p. 89°. When distilled, the oxime yields *6-phenyl-2-nonylpyridine*, $C_{20}H_{27}N$, which is a pale yellow oil, b. p. 165—170°/30 mm.; the *platinichloride* $(C_{20}H_{27}N)_2,H_2PtCl_6$, crystallises in pale red needles, m. p. 201°.

α-Piperonylidenemethyl nonyl ketone, $CH_2O_2:C_6H_3\cdot CH:CH\cdot CO\cdot C_9H_{19}$, crystallises in pale yellow, felted needles, m. p. 56°; *semicarbazone*, $C_{20}H_{29}O_3N_3$, forms colourless needles, m. p. 151°. p-*Methylstyryl nonyl ketone*, $C_6H_4Me\cdot CH:CH\cdot CO\cdot C_9H_{19}$, crystallises in plates, m. p. 129°. p-*Methoxystyryl nonyl ketone*, $OMe\cdot C_6H_4\cdot CH:CH\cdot CO\cdot C_9H_{19}$, forms colourless, glistening plates, m. p. 63°, and yields a *semicarbazone*, $C_{20}H_{31}O_2N_3$, in the form of pale yellow needles, m. p. 114°. p-iso-*Propylstyryl nonyl ketone*, $C_3H_7\cdot C_6H_4\cdot CH:CH\cdot CO\cdot C_9H_{19}$, forms soft, colourless needles, m. p. 144°.

The *semicarbazone* of α-naphthyl methyl ketone, $C_{13}H_{13}ON_3$, forms colourless crystals, m. p. 205°. *Cinnamylidenemethyl α-naphthyl ketone*, $CHPh:CH\cdot CH:CH\cdot CO\cdot C_{10}H_7$, is an oil; the *oxime*, $C_{21}H_{17}ON$, crystallises in yellow needles, m. p. 123°, and, when distilled, yields a small amount of *6-phenyl-2-α-naphthylpyridine*, $C_{21}H_{15}N$, as a pale yellow oil, b. p. 190—192°/12 mm., but the *platinichloride* of which crystallises in pale red needles, m. p. 109°.

p-*Nitrostyryl α-naphthyl ketone*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot C_{10}H_7$, forms yellow needles, m. p. 131°.

The *semicarbazone* of *p*-acetylanisole, $C_{10}H_{10}O_2N_3$, forms colourless plates, m. p. 198°. *Cinnamylidenemethyl* p-*methoxyphenyl ketone*,

$$CHPh:CH\cdot CH:CH\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallises in yellow, felted needles, m. p. 93°; its *semicarbazone*, $C_{19}H_{18}O_2N_3$, has m. p. 189°, and its *oxime*, $C_{18}H_{17}O_2N$, forms yellow needles, m. p. 147°, and, when distilled, yields *2-phenyl-6-anisylpyridine*, $C_{18}H_{15}ON$, as pale yellow needles, m. p. 119°.

Piperonylidene-p-*methoxyacetophenone*,

$$CH_2O_2:C_6H_3\cdot CH:CH\cdot CO\cdot C_6H_4\cdot OMe,$$

forms pale yellow, glistening needles, m. p. 129°, and *cinnamylidenemethyl benzyl ketone*, $CHPh:CH\cdot CH:CH\cdot CO\cdot CH_2Ph$, similar needles, m. p. 119°. J. J. S.

The Friedel-Crafts' Reaction with Chlorides of Unsaturated Acids. ELMER P. KOHLER, GERTRUDE L. HERITAGE, and M. C. BURNLEY (*Amer. Chem. J.*, 1910, **44**, 60—76. Compare Abstr., 1907, i, 1050; 1909, i, 938).—Cinnamoyl chloride and excess of benzene in carbon disulphide react with aluminium chloride to form ββ-diphenyl-

propiophenone, 3-keto-1-phenyl-2 : 3-dihydroindene, and β-chloro-β-phenylpropiophenone; styryl phenyl ketone cannot be isolated. Under similar conditions, cinnamoyl chloride reacts with bromobenzene to form about 25% of p-*bromophenyl styryl ketone*, $CHPh:CH\cdot CO\cdot C_6H_4Br$, m. p. 100—101°, and 6-*bromo*-3-*keto*-1-*phenyl*-2 : 3-*dihydroindene*, $C_6H_3Br<\substack{CHPh\\ -CO-}>CH_2$, m. p. 60—61°, in 30—35% yield. With anisole or phenetole, cinnamoyl chloride yields only the expected unsaturated ketones.

αβ-Dibromo-β-phenylpropionyl chloride is conveniently prepared by adding phosphorus pentachloride to a suspension of dibromocinnamic acid in phosphoryl chloride, removing the chlorides of phosphorus at 150—160° under diminished pressure, and crystallising the residue from carbon disulphide and petroleum. In carbon disulphide cooled by a freezing mixture, the chloride reacts with aluminium chloride alone, hydrogen bromide and a little chloride being evolved, and phenylacetylene, bromostyrene, *p*-bromocinnamic acid, cinnamic acid, α-bromocinnamic acid, and a small quantity of other unidentified products being formed.

αβ-Dibromo-β-phenylpropionyl chloride, benzene, and aluminium chloride react in carbon disulphide at −20° to form a substance, m. p. 89—90°, which is not dibromophenylpropiophenone, as stated by Collet, but 2-bromo-3-keto-1-phenyl-2 : 3-dihydroindene, the *semicarbazone* of which has m. p. 212° (decomp.). With bromobenzene, dibromophenylpropionyl chloride yields, in addition to a large quantity of acid by-products due to the reaction between the acid chloride and the aluminium chloride, 2 : 6-*dibromo*-3-*keto*-1-*phenyl*-2 : 3-*dihydroindene*, m. p. 143—144°, and an isomeric substance, m. p. 86°, which is probably a stereoisomeride, since both substances yield p-*bromo*-o-*benzoylbenzoic acid*, m. p. 174°, by oxidation by potassium permanganate in acetone, and the substance of higher m. p. is converted almost quantitatively into the other at its m. p. C. S.

Acetylenic Ketones. ÉMILE ANDRÉ (*Compt. rend.*, 1910, **151**, 75—78).—In the preparation of acetylenic ketones from the sodium derivatives of unsaturated hydrocarbons, better yields are obtained by using an acid bromide instead of the acid chloride. iso*Valerylphenylacetylene*, $CPh:C\cdot CO\cdot CH_2Pr^\beta$, has b. p. 149—151°/12 mm., D^{20} 0·969, n_D^{20} 1·5405. *Hexoylphenylacetylene*, $C_5H_{11}\cdot CO\cdot C:CPh$, m. p. 14—15°, b. p. 170—172°/12 mm., D^{20} 0·965, n_D^{20} 1·5352, was prepared from *hexoyl bromide*, b. p. 175—176°. The ketones have also been prepared by oxidising the corresponding secondary alcohols (Moureu, Abstr., 1902, i, 289) with chromic acid in acetic acid solution (compare Dupont, this vol., i, 456). The molecular refractions for five ketonic derivatives of phenylacetylene have been determined, and found to exceed the calculated values by about three units. W. O. W.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. VI. Ketochlorides of Dianisylideneacetone [Di-*p*-methoxystyryl Ketone] and Dicinnamylideneacetone. FRITZ STRAUS [with GEORG LUTZ and WERNER HÜSSY] (*Annalen*, 1910, **374**, 40—90. Compare this vol., i, 119).—In the main, an amplifica-

tion and extension of the investigations of Straus and Ecker (compare Abstr., 1906, i, 859). Di-*p*-methoxystyryl ketone forms *additive* compounds with the following substances: mercuric chloride, deep yellow, slender, soft needles; calcium chloride, bright yellow powder; phosphoryl chloride, dark reddish-brown oil. The ketone, when treated with phosphorus pentachloride in carbon disulphide, yields the *additive* product, $(OMe\cdot C_6H_4\cdot CH\colon CH)_2CCl_2,PCl_5$, a green, crystalline powder, an ethereal solution of which when treated with ice-water and subsequently with sodium hydrogen carbonate and light petroleum yields the *hydrochloride* of $\beta\beta$-dichloro-$\alpha\gamma$-dianisylidenepropane,

$$(OMe\cdot C_6H_4\cdot CH\colon CH)_2CCl_2,HCl,$$

a dark green powder with a metallic reflex; the ketochloride is obtained from the hydrochloride by boiling with dry petroleum ether, and crystallises in faintly yellow, silvery leaflets, m. p. 91—92° (compare Staudinger, Abstr., 1909, i, 906). $\beta\beta$-Dichloro-$\alpha\gamma$-dianisylidenepropane is converted by water into the *chlorocarbinol*,

$$(OMe\cdot C_6H_4\cdot CH\colon CH)_2CCl\cdot OH(?),$$

an unstable oil. *Additive* compounds of the ketochloride with the following substances have been prepared: mercuric chloride,

$$C_{19}H_{18}O_2Cl_2,4HgCl_2,$$

violet crystals with a green reflex; thionyl chloride,

$$C_{19}H_{18}O_2Cl_2,SOCl_2,$$

green powder; phosphoryl chloride, intensely green oil; carbonyl chloride, unstable, green powder; sulphur dioxide, $3C_{19}H_{18}O_2Cl_2,2SO_2$, a stable, green, crystalline powder; acetonitrile, propionitrile, benzonitrile, and benzyl cyanide, substances soluble in excess to pale blue solutions. The *sulphate*,

$$(OMe\cdot C_6H_4\cdot CH\colon CH)_2CCl\cdot OSO_3H,xH_2SO_4,$$

prepared by adding sulphuric acid to a solution of the ketochloride in methyl sulphate, crystallises in glistening, green leaflets, The ketochloride is converted by chlorine into the dichloride, m. p. 107—108° (compare Straus and Ecker, *loc. cit.*), which is slowly attacked by a solution of chlorine in tetrachloromethane, but apparently not by bromine in chloroform. The ketochloride or its dichloride, when acted on by methyl alcohol, yields the *methyl ether*,

$$(OMe\cdot C_6H_4\cdot CH\colon CH)_2CCl\cdot OMe,$$

of the corresponding chloro-carbinol, which crystallises in tufts of white needles or leaflets, m. p. 87—88°, and dissolves in concentrated sulphuric acid or liquid sulphur dioxide, forming blue solutions. Hydrogen chloride converts the methyl ether, dissolved in light petroleum, into the hydrochloride of the corresponding ketochloride, but when the solvent is benzene or carbon disulphide, the ether is converted into the hydrochloride of the corresponding ketone. The action of methyl alcohol on the ketochloride dichloride leads to the formation of two *methyl ethers* having the composition $C_{20}H_{21}O_3Cl_3$, which are probably cis- and trans-isomerides; the one crystallises in slender, white leaflets, m. p. 99—100°, whilst the other forms colourless needles, m. p. 80—81°; both isomerides are decomposed slowly by methyl alcohol with the elimination of chlorine, and when acted on by active aluminium in an alcoholic solution of sodium methoxide yield the methyl ether of 4 : 4′-dimethoxydicinnamenyl-

chlorocarbinol. The ketochloride dichloride, when treated with silver oxide, yields the *dichloride* of the chlorocarbinol,

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHCl\cdot CCl(OH)\cdot CH\colon CH\cdot C_6H_4\cdot OMe,$$

which crystallises in felted, slender, white needles, m. p. 121°.

Dicinnamylideneacetone, when acted on by phosphorus pentachloride under suitable conditions, yields the corresponding *ketochloride*, $(CHPh\colon CH\cdot CH\colon CH)_2CCl_2$, which forms colourless crystals, m. p. 114·5°, and when treated with chlorine in tetrachloromethane yields the *tetrachloride*,

$$CHPh\colon CH\cdot CH\colon CH\cdot CCl_2\cdot CHCl\cdot CHCl\cdot CHCl\cdot CHPhCl,$$

which is also obtained by boiling the ketone dissolved in a mixture of benzene and chloroform with phosphorus pentachloride, and forms colourless, compact crystals, m. p. 172° (decomp.). The tetrachloride combines with further quantities of chlorine, forming mixtures of *hexa-* and *octa*-chlorides. The ketochloride also combines with bromine, yielding a *hexabromide*, $C_{21}H_{18}Cl_2Br_6$, which crystallises in tufts of small, colourless prisms decomposing at 219°. The ketochloride forms *additive* products with the following substances: mercuric chloride, $C_{21}H_{18}Cl_2,2HgCl_2$, metallic, green powder; phosphorus pentachloride, $C_{21}H_{18}Cl_2,PCl_5,C_6H_6$, glistening, green, slender leaflets; phosphoryl chloride, glistening, green leaflets; stannic chloride, dark green powder with a green reflex; acetyl chloride, thionyl chloride, and liquid sulphur dioxide, products forming green solutions. The ketochloride also forms green *salts* with sulphuric acid, nitric acid, and hydrogen chloride. The following derivatives of the ketochloride are prepared by methods similar to those already described: *chlorocarbinol*, $C_{20}H_{18}\colon CCl\cdot OH$, long, white needles, m. p. 122°; *methyl ether*, $C_{20}H_{18}\colon CCl\cdot OMe$, slender, white needles or glistening leaflets, m. p. 120·5°. W. H. G.

Dibenzylideneacetone (Distyryl Ketone) and Triphenylmethane. VII. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. II. FRITZ STRAUS [and, in part, with JEAN B. KRIER and GEORG LUTZ] (*Annalen*, 1910, **374**, 121—198. Compare this vol., i, 119 and preceding abstract; Straus and Ecker, Abstr., 1906, i, 859; Strauss and Caspari, 1907, i, 609; Straus and Ackermann, 1909, i, 489; Straus and Hüssy, *ibid.*, 490).—The ketohalides of *pp*-dimethoxybenzylideneacetophenone have been investigated. They resemble the halides already described, but are more reactive, owing to the presence of the methoxy-substituents. They also yield intensely coloured perbromides and periodides, analogous to those derived from the triphenylmethyl halides. Unlike most of the examples studied previously, it is found that the bromide has a lower m. p. than the chloride.

The chlorobromides have been prepared by the following methods:

$$(1)\ R_1R_2CBrBr \longrightarrow R_1R_2CBr\cdot OH \longrightarrow R_1R_2CBrCl$$
$$(2)\ R_1R_2CClCl \longrightarrow R_1R_2CCl\cdot OH \longrightarrow R_1R_2CClBr,$$

and the products obtained have been found to be identical. This has been proved by determining the amounts of halogen hydracids liberated

by the action of hydroxylic reagents, such as water and methyl alcohol, on the products. The amount of hydrogen bromide formed is much greater than the amount of hydrogen chloride (20%).

It is pointed out that the relative amounts of the two halogen hydracids vary with the constitution of the ketone from which the ketohalides are derived, and thus each case is characterised by a specific equilibrium of the two valency forms.

Water and methyl alcohol transform the ketodichlorides into the corresponding chlorocarbinol and its methyl ether, but these are spontaneously decomposed into the ketone, probably owing to the intermediate formation of an oxonium derivative: $R_1R_2CCl{\cdot}OMe \longrightarrow R_1R_2C{:}O{<}^{Cl}_{Me} \longrightarrow R_1R_2C{:}O$.

It is found that the keto-dichloride and -dibromide affect one another in solution. When freshly mixed, the solution yields molecular proportions of hydrochloric and hydrobromic acids, but the amount of hydrobromic acid increases at the expense of the hydrochloric, until an equilibrium is established, which is identical with that obtained when a solution of the ketochlorobromide has been kept for some time. The conclusion is drawn that the chlorobromide in solution decomposes to a slight extent into molecular quantities of dichloride and dibromide, and that the three halogen derivatives are present in solution in a state of equilibrium:

$$R_1R_2CCl_2 + R_1R_2CBr_2 \rightleftarrows 2R_1R_2CClBr.$$

When evaporated the solution yields a product with all the properties of the chlorobromide, and this is its simplest method of formation; after purification, a solution of the product gives the usual relative amounts of hydrochloric and hydrobromic acids, but in the course of time returns to the above-mentioned equilibrium. Coloured intermediate products are not formed, and all the reactions are attributed to decompositions into colourless ions (compare Hantzsch and Meyer, this vol., i, 238): $2CR_1R_2ClBr \rightleftarrows CR_1R_2Cl^{\cdot} + CR_1R_2Br^{\cdot} + Cl' + Br' \rightleftarrows CR_1R_2Cl_2 + CR_1R_2Br_2$.

The solid chlorobromide is regarded as the pure compound, CR_1R_2ClBr, and dissociation is supposed to take place on fusion or solution.

The formation of the ketodibromide from the chlorobromide and bromine or hydrogen-bromide is not merely due to the relative amounts of the valency isomerides present, but also depends on the rapidity with which the equilibrium between the ketohalides is attained, and this varies with different ketones.

Di-p-methoxyphenyl styryl ketone, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$ obtained by condensing acetylanisole (Abstr., 1890, 963) with anisaldehyde in the presence of sodium ethoxide (5% solution), crystallises in yellow prisms, m. p. 101—102°, and gives a reddish-yellow coloration with concentrated sulphuric acid. The *compound* with mercuric chloride, $C_{17}H_{16}O_3,HgCl_2$, forms golden-yellow needles, m. p. 150°, and is much more stable than the corresponding derivative of distyryl ketone. The *dibromide*, $OMe{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, forms snow-white crystals, m. p. 140° (decomp.), and when boiled with ten times its weight of methyl alcohol for twenty minutes yields the

methyl ether, $OMe\cdot C_6H_4\cdot CH(OMe)\cdot CHBr\cdot CO\cdot C_6H_4\cdot OMe$, as colourless needles, m. p. 108—109°, which dissolve in concentrated sulphuric acid to cherry-red solutions.

The *ketodichloride*, p-*methoxyphenyl*-p-*methoxystyryldichloromethane*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl_2\cdot C_6H_4\cdot OMe$, is best isolated as its additive *compound* with phosphorus pentachloride, $C_{17}H_{16}O_2Cl_2,PCl_5$, which forms steel-blue crystals. The ketodichloride crystallises from a mixture of carbon disulphide and light petroleum in brilliant colourless, compact prisms, melting at 78° to a green liquid. The *compound*, $C_{17}H_{16}O_2Cl_2,4HgCl_2$, forms brownish-violet needles, and is most useful for characterising the chloride. The *hydrochloride*, $C_{17}H_{16}O_2Cl_2,HCl$, forms slender, blue needles, and the *periodide*, $C_{17}H_{16}O_2Cl_2I_4$, dark crystals, m. p. 81—83°, which are partially decomposed by most solvents. The *sulphate* has not been obtained crystalline, and an additive compound with carbon disulphide has not been isolated. The ketochloride reacts with a carbon tetrachloride solution of chlorine, yielding the *additive* compound,

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHCl\cdot CCl_2\cdot C_6H_4\cdot OMe,$$

in the form of an unstable oil, which appears to be identical with the product obtained by the action of an excess of phosphorus pentachloride on a benzene solution of the ketone. A solution of bromine in carbon disulphide yields the *perbromide*, $C_{17}H_{16}O_2ClBr,Br_2$, in the form of a green precipitate, m. p. 120° (decomp.).

Thionyl chloride and phosphoryl chloride yield precipitates, but phosphorus trichloride, acetyl chloride, and nitriles do not. Nitriles yield pale blue solutions, and liquid sulphur dioxide an intense violet solution.

p-Chlorophenyl-*p*-chlorostyryldichloromethane (Abstr., 1909, i, 489) yields a *dichloride*, *αγ-di*-p-*chlorophenyl-ααβγ-tetrachloropropane*,

$$C_6H_4Cl\cdot CHCl\cdot CHCl\cdot CCl_2\cdot C_6H_4Cl,$$

which crystallises from methyl alcohol in slender, colourless needles, m. p. 101°. The compound is formed slowly, and when reduced with active aluminium and sodium methoxide dissolved in methyl alcohol yields 4 : 4′-*dichlorophenylbenzylacetylene*, $C_6H_4Cl\cdot C{:}C\cdot CH_2\cdot C_6H_4Cl$, as colourless plates, m. p. 80—80·5°.

p-Methoxyphenyl-*p*-methoxystyryldichloromethane reacts readily with water, and also with methyl alcohol, yielding 4 : 4′-*dimethoxyphenylstyrylchlorocarbinol*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl(OH)\cdot C_6H_4\cdot OMe$, and its *methyl ether*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CCl(OMe)\cdot C_6H_4\cdot OMe$. The carbinol crystallises as colourless, felted needles, m. p. 75—76°, and the methyl ether as glistening, colourless plates, m. p. 44—45°. Both compounds are extremely unstable, and in their preparation it is necessary to avoid light and all traces of acid. The carbinol reacts readily with concentrated hydrochloric acid, regenerating the ketodichloride, and the methyl ether with glacial acetic acid yields the ketone.

The *ketodibromide*, 4 : 4′-*dimethoxyphenylstyryldibromomethane*, cannot be prepared by the action of phosphorus pentabromide on the ketone or its hydrobromide, but can be obtained by the action of phosphorus tribromide on a benzene solution of the ketone. The reaction is slow, and is of use only with ketones containing a reactive carbonyl group, especially those containing methoxy-substituents. The ketobromide is

best isolated as its complex with mercuric bromide, or, in certain cases, as its additive compound with bromine, and can be obtained from the mercuric bromide compound by conversion into the bromocarbinol and treatment with hydrobromic acid.

4 : 4′-*Dimethoxyphenylstyrylbromocarbinol*,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot CBr(OH)\cdot C_6H_4\cdot Me,$$

crystallises in long, colourless, felted needles, m. p. 83—84°, is only moderately stable, and is immediately decomposed by mineral acids, regenerating the ketone; with hydrobromic acid it yields 4 : 4′-*dimethoxyphenylstyryldibromomethane*,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot CBr_2\cdot C_6H_4\cdot OMe,$$

which can be crystallised with some difficulty from a mixture of carbon disulphide and light petroleum. It forms long, lemon-yellow prisms, m. p. 64°, to a green liquid, and gives rises to the following derivatives: $C_{17}H_{16}O_2Br_2,3HgBr_2$, small, violet needles; *perbromide*, $C_{17}H_{16}O_2Br_2,Br_2$, green crystals, m. p. 128—130°, can be obtained by the action of either bromine or phosphorus pentabromide on the ketodibromide; *periodide*, $C_{17}H_{16}O_2Br_2,I_4$, green crystals, m. p. 104—106° (decomp.); *hydrobromide*, $C_{17}H_{16}O_2Br_2,HBr$, steel-blue needles, m. p. 90—95°; *sulphate*, green, glistening needles; *nitrate*, steel-blue, sparingly soluble needles; $C_{17}H_{16}O_2Br_2,SO_2$, bluish-green, glistening crystals. The ketodibromide also yields bluish-green, crystalline precipitates with solutions of zinc chloride, ferric chloride, and mercuric chloride in concentrated hydrochloric acid. Water or silver oxide and ether transform the ketodibromide into the bromocarbinol, glacial acetic acid transforms it into the ketone, and methyl alcohol transforms first into the methyl ether of the bromocarbinol (one to two minutes) and ultimately (eight hours) into the ketone. The *methyl ether*, $OMe\cdot C_6H_4\cdot CH:CH\cdot CBr(OMe)\cdot C_6H_4\cdot OMe$, crystallises in colourless, glistening plates, m. p. 39·5—40·5°.

Phosphorus tribromide reacts with a boiling ethereal solution of di-*p*-methoxystyryl ketone, giving a quantitative yield of the *hydrobromide* of the ketone, $C_{19}H_{18}O_3,HBr$, as a dark reddish-violet precipitate. Phosphorus tribromide, when boiled with a benzene solution of di-*p*-methoxystyryl ketone, yields *di*-p-*methoxystyryldibromomethane*, which can be isolated as its green complex with mercuric bromide. When this complex is shaken with a solution of potassium bromide in 66% methyl alcohol, *di*-p-*methoxystyrylbromocarbinyl methyl ether*, $(OMe\cdot C_6H_4\cdot CH:CH)_2CBr\cdot OMe$, is formed. It crystallises in snow-white plates, m. p. 102—103°, and its solution in concentrated sulphuric acid has a pure blue colour.

Phosphorus pentabromide reacts with a carbon disulphide solution of distyryl ketone or its hydrobromide, yielding the same products as does bromine itself (compare Vörlander and Siebert, Abstr., 1904, i, 900). With phosphorus tribromide, the ketodibromide is formed, and this can be isolated as the *tetrabromo*-compound,

$$CHBrPh\cdot CHBr\cdot CBr_2\cdot CH:CHPh,$$

m. p. 170° (decomp.).

Di p-*methoxyphenylstyrylchlorobromomethane*,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot CBrCl\cdot C_6H_4\cdot OMe,$$

is more readily obtained by the action of hydrochloric acid on the

bromocarbinol than by that of hydrobromic acid on the chlorocarbinol, as the latter reaction is accompanied by side reactions. It crystallises in brilliant, lemon-yellow prisms, m. p. 71°, to a green liquid. Its addition to the ketodibromide raises the m. p. The *complex*,

$$C_{17}H_{16}O_2ClBr,2HgBr_2,$$

forms reddish-violet needles; the *perbromide*, $C_{17}H_{16}O_2ClBr,Br_2$, has m. p. 122° (decomp.); the *periodide* forms a brilliant green, crystalline precipitate, m. p. 102—104° (decomp), and the *hydrobromide*, steel-blue needles, and in its preparation a portion of the chlorine becomes replaced by bromine. The additive compound with sulphur dioxide forms green, metallic, glistening crystals, which are unstable. The ketodibromide and the chlorobromide are not affected when shaken with dry benzene and silver chloride. J. J. S.

Terpenes and Ethereal Oils. CII. OTTO WALLACH (*Annalen*, 1910, **374**, 217—235).—I. *Preparation of Hydroxy-ketones and* 1 : 2-*Glycols from the Nitrosochlorides of Semicyclic Hydrocarbons.*—Both of the nitrosochlorides derived from 1-methyl-4-ethylidene*cyclo*hexane react with a mixture of anhydrous sodium acetate and glacial acetic acid at 63—70°, yielding the *oxime* of 4-*acetoxy*-1-*methyl*cyclo*hexyl methyl ketone*, $CHMe<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}>C(OAc)\cdot CMe\colon N\cdot OH$, m. p. 111—112°, together with the oxime of *p*-acetylmethyl*cyclo*hexene; the latter compound is also formed when the oxime melting at 111—112° is distilled.

When the oxime is hydrolysed with 5% sulphuric acid, 4-*hydroxy*-4-*acetylhexahydrotoluene* (4-*hydroxy*-1-*methyl*cyclo*hexyl methyl ketone*), $CHMe<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}>CAc\cdot OH$, is formed. It has b. p. 223—224° and m. p. 21—22°, and is only sparingly volatile in steam; its *semicarbazone* crystallises in plates, m. p. 219—220°, and its *oxime* has m. p. 128°. When boiled with 20% sulphuric acid, the hydroxy-ketone yields *p*-acetylmethyl*cyclo*hexene, and when treated with magnesium methyl iodide yields *menthan*-4 : 8-*diol* (4 : 8-*terpin*),

$$CHMe<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}>C(OH)\cdot CMe_2\cdot OH,$$

which exists in two stereoisomeric forms, melting respectively at 97—98° and 82—83°. The less fusible compound has b. p. 245°, and yields a liquid bromide; when oxidised, it yields *p*-methyl*cyclo*hexanone. The glycol, m. p. 82—83°, is more readily soluble than its isomeride, and both compounds are readily volatile in steam.

II. *The Terpinene Question* (compare Wallach, Abstr., 1907, i, 1058; 1908, i, 813; Auwers and Heyden, Abstr., 1909, i, 593; Müller, Walbaum, and Müller, *Schimmel's Ber.*, 1909, ii, 16, 33).—A brief summary of researches on terpinenes. It is pointed out that all terpinenes, even that obtained from terpinene dihydrochloride, contain both $\Delta^{1:3}$-dihydro-*p*-cymene and the isomeric $\Delta^{1:4}$-compound. The presence of the former has been established by its conversion into $\alpha\delta$-dihydroxy-α-methyl-δ'-*iso*propyladipic acid, and it is this constituent of the terpinene which yields the nitrosite, m. p. 155°. The presence of $\Delta^{1:4}$-dihydro-*p*-cymene has been proved by its oxidation to the

erythritol (1 : 2 : 3 : 4-tetrahydroxyterpane), which can be transformed by loss of water into a mixture of carvacrol and thymol (Gildmeister and Müller, *Schimmel's Ber.*, 1909, ii, 16). α-Terpinene $= \Delta^{1:3}$-dihydro-*p*-cymene $= \Delta^{1:3}$-menthadiene = carvenene (Semmler). β-Terpinene $= \Delta^{1(7):4}$-menthadiene; γ-terpinene $= \Delta^{1:4}$-dihydro-*p*-cymene $= \Delta^{1:4}$-menthadiene = *iso*carvenene (Semmler). So far, neither $\Delta^{1:3}$- nor $\Delta^{1:4}$-menthadiene has been obtained free from its isomeride, and the same appears to hold good for all doubly-unsaturated cyclic hydrocarbons.

J. J. S.

pp-**Dibromobenzil.** HEINRICH BILTZ, H. EDLEFSEN, and KARL SEYDEL (*Ber.*, 1910, **43**, 1815—1820. Compare Biltz, Abstr., 1908, i, 575; 1909, i, 839).—Di-*p*-bromobenzil yields a *monoxime*,

$$C_{14}H_9O_2NBr_2,$$

in the form of minute, colourless needles, m. p. 159—160°, and a *phenylhydrazone*, $C_{20}H_{14}ON_2Br_2$, m. p. 189°. It does not yield a semicarbazone, but forms *3-oxy-5 : 6-di-p-bromophenyl-2 : 1 : 4-triazine*, $\begin{matrix} C_6H_4Br\cdot C{:}N\cdot CO \\ C_6H_4Br\cdot C{:}N\cdot NH \end{matrix}$, when heated with semicarbazide hydrochloride and dilute acetic acid. This crystallises in colourless needles, m. p. 253°, and yields a *sodium* derivative, $C_{15}H_8ON_3Br_2Na$, in the form of pale yellow prisms, and an *acetyl* derivative, $C_{17}H_{11}O_2N_3Br_2$, in the form of hexagonal, colourless plates, m. p. 282°, which are readily hydrolysed.

Di-p-bromobenzilic acid, $OH\cdot C(C_6H_4Br)_2\cdot CO_2H$, prepared by the action of an alcoholic solution of sodium ethoxide on the dibromobenzil at the ordinary temperature, crystallises from a mixture of chloroform and light petroleum in needles, m. p. 108—110°, and when heated with carbamide at 220° yields 5 : 5-dibromophenylhydantoin. When heated for three to four hours at 180°, the acid loses carbon dioxide and yields *di-p-bromobenzhydrol*, $OH\cdot CH(C_6H_4Br)_2$, which crystallises in glistening, colourless plates, m. p. 174—175°.

Di-p-bromodiphenylacetic acid, $CH(C_6H_4Br)_2\cdot CO_2H$, obtained by reducing the benzilic acid with hydriodic acid and red phosphorus in the presence of acetic acid, crystallises in needles, m. p. 187—188°.

Dibromodeoxybenzoin, $C_6H_4Br\cdot CO\cdot CH_2\cdot C_6H_4Br$, obtained by reducing dibromobenzil with zinc dust and glacial acetic acid, crystallises in long, brittle needles, m. p. 141—142°, and does not yield an oxime, a phenylhydrazone, or a semicarbazone. J. J. S.

Acylated Aminoanthraquinones and Anthraquinone Mercaptans and their Behaviour on Vegetable Fibres. CHR. SEER and R. WEITZENBÖCK (*Monatsh.*, 1910, **31**, 371—377).—Recently vat-dyes of the anthraquinone series have been obtained by the action of benzoyl chloride on aminoanthraquinones dissolved in nitrobenzene (*Chem. Zeit.*, 1909, No. 108). The authors have now prepared acylated aminoanthraquinones in a similar manner, and find that they are pronounced vat-dyes, giving on unmordanted cotton tones which are deeper than those of the analogous benzoylated compounds. The *amide*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_3\cdot NH\cdot CO\cdot C_6H_3{<}^{CO}_{CO}{>}C_6H_4$, m. p. 350°, ob-

tained by heating 2-aminoanthraquinone and the chloride of anthraquinone-2-carboxylic acid in nitrobenzene for half an hour, forms pale yellow crystals, and in the hyposulphite vat produces feeble yellow tones on unmordanted cotton. The *amides*, obtained from the same acid chloride and 1 : 5-, 1 : 3-, and 1 : 8-diaminoanthraquinones respectively, produce on unmordanted cotton in the hyposulphite vat brown to brownish shades, which are changed to brown to brick-red by atmospheric oxidation. The *amide*, $C_{28}H_{15}O_6NS$, m. p. 257°, obtained from 1-aminoanthraquinone and anthraquinone-2-sulphonyl chloride, yields a dark red vat, which produces brown shades changing to faint greyish-green by oxidation. 1 : 5-Diaminoanthraquinone and anthraquinone-2-sulphonyl chloride yield the *amide*,

$$C_{14}H_6O_2(NH\cdot SO_2\cdot C_6H_3{<}^{CO}_{CO}{>}C_6H_4)_2,$$

m. p. 391°, the vat of which is dark red, producing faint red shades changing to light yellow by oxidation.

1 : 5-Diaminoanthraquinone and picryl chloride in nitrobenzene yield *dipicryl*-1 : 5-*diaminoanthraquinone*,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3{<}^{CO}_{CO}{>}C_6H_3\cdot NH\cdot C_6H_2(NO_2)_3,$$

which decomposes above 340°, and forms a brown vat in alkaline hyposulphite, which produces dark green shades on unmordanted cotton; these shades are changed by oxidation to violet, which are turned brown by the addition of dilute hydrochloric acid.

Anthraquinone-1-thiol and benzoyl chloride in nitrobenzene yield *benzoylanthraquinone*-1-*thiol*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_3\cdot SBz$, m. p. 208°, which forms yellow crystals, and has not the slightest affinity for vegetable fibres. C. S.

Action of Benzyl Chloride and of Monochloroacetic Acid on Aminoanthraquinones. CHR. SEER and R. WEITZENBÖCK (*Monatsh.*, 1910, **31**, 379—386).—In view of the fact that the introduction of acyl groups into the amino-groups of aminoanthraquinones converts these coloured but non-dyeing substances into strong dyes, the effect of the introduction of benzyl, *p*-chlorobenzyl, and glycino-groups has been examined. The products do not possess the character of vat-dyes.

1-*Benzylaminoanthraquinone*, m. p. 189°, obtained from 1-aminoanthraquinone and benzyl chloride at 170—175°, forms red needles, and is reduced by alkaline hyposulphite to the corresponding dihydroanthraquinone. 1-*Anthraquinonylglycine*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3\cdot NH\cdot CH_2\cdot CO_2H,$$

m. p. 218—226° (decomp.), obtained from 1-aminoanthraquinone, anhydrous sodium acetate, and chloroacetic acid at 170°, is a brick-red powder. 1 : 5-*Diglycinoanthraquinone*,

$$CO_2H\cdot CH_2\cdot NH\cdot C_6H_3{<}^{CO}_{CO}{>}C_6H_3\cdot NH\cdot CH_2\cdot CO_2H,$$

obtained from 1 : 5-diaminoanthraquinone in a similar manner, is a dark red powder, which dyes wool directly, and dissolves in alkalis with an extremely deep reddish-violet colour.

1 : 5-*Dibenzylaminoanthraquinone*, m. p. 225°, and 1 : 5-*di*-p-*chlorobenzylaminoanthraquinone*, m. p. 271—272°, are remarkable in that they are not converted into the corresponding dihydroanthraquinones by alkaline reducing agents. *Dibenzoyl*-1 : 5-*dibenzylaminoanthraquinone*, $C_{42}H_{30}O_4N_2$, m. p. 293°, prepared from 1 : 5-dibenzylaminoanthraquinone and benzoyl chloride at 90—100°, crystallises in red leaflets. C. S.

Relation between Molecular Constitution and Odour. GÉZA AUSTERWEIL and G. COCHIN (*Compt. rend.*, 1910, **150**, 1693—1695).—Citronellol, 1-methylcitronellol, and 1 : 1-*dimethylcitronellol* have distinct rose-like odours. The latter compound was obtained by oxidising 1-methylcitronellol and treating the resulting ketone by Grignard's method; it has b. p. 113—116°/24 mm., $[\alpha]_D$ $-11°38'$. 1-*Ethylcitronellol*, b. p. 125—130°/22 mm., $[\alpha]_D$ $-11°26'$, and 1 : 1-*diethylcitronellol*, b. p. 119—123°/20 mm., $[\alpha]_D$ $-13°25'$, have well-marked, rose-like odours. The odour is less distinct in 1-*propylcitronellol*, b. p. 118—122°/22 mm., and 1-*butylcitronellol*, b. p. 105—108°/16 mm. Introduction of a phenyl group intensifies the odour; 1-*phenylcitronellol* has b. p. 102—104°/12 mm.

An odour of roses appears to be associated with the presence of the group $-CH_2 \cdot CRR' \cdot OH$; the presence of an ethylenic linking also appears to be essential. W. O. W.

A New Tertiary Menthol; Conversion of Pinene into Menthene. AUGUSTE BÉHAL (*Compt. rend.*, 1910, **150**, 1762—1765).—Haller and Martine (Abstr., 1905, i, 533) obtained hexahydrocymene by the reduction of terpineol; employing the same method, but under different conditions, the present author has converted terpineol into a tertiary *menthol*, $CHMe{<}{}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}CH \cdot CMe_2 \cdot OH$. The product is optically inactive, and does not appear to be a mixture of *cis*- and *trans*-isomerides; it has b. p. 99—100°/17 mm., 206—208° under atmospheric pressure; D^{20} 0·912; n_D 1·46874. The *phenylurethane* has m. p. 94—95°; the *acetate* has b. p. 104°/16 mm. Acetic acid in presence of sulphuric acid transforms the menthol into $\Delta^{4(8)}$-menthene (Wallach, Abstr., 1905, i, 407; Auwers, this vol., i, 122). Oxidation with mercuric oxide and iodine, followed by treatment with silver nitrate, converts this hydrocarbon into menthone.

W. O. W.

Constitution of Fenchone. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], **7**, 542—548).—A résumé of work already published (Abstr., 1908, i, 193). The fenchone used was isolated by fractional distillation from the crude fenchone obtained from fennel oil. On treatment with sodamide until no further action took place, a residue containing camphor was obtained.

T. A. H.

Constitution of Fenchone. II. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], **7**, 683—687).—A résumé of

work already published in part (Abstr., 1908, i, 193; 1909, i, 497, 595). The following new data are given. Dihydrofencholenic acid, b. p. 162—165°/22 mm., obtained by hydrolysis of the amide with 30% potassium hydroxide in alcohol, does not solidify when pure (compare Semmler, Abstr., 1906, i, 681). The *chloride* has b. p. 105°/20 mm. The *anhydride*, b. p. 205—210°/20 mm., D^4 0·9841, obtained by warming the acid with acetic anhydride, is a colourless, thick liquid.

Dihydrofencholenamide, $C_9H_{17}\cdot CO\cdot NH_2$, on treatment with bromine and potassium hydroxide, gives di*apo*fenchylcarbamide,

$$CO(NH\cdot C_9H_{17})_2$$

(Abstr., 1908, i, 193), but if the alkali is replaced by sodium methoxide, the corresponding *methylurethane*, $C_{11}H_{21}O_2N$, b. p. 142°/23 mm., a colourless liquid of pleasant odour, is obtained. This is very stable to alkalis, but on prolonged heating with 30% potassium hydroxide in alcohol at 150° it furnishes apo*fenchylamine*,

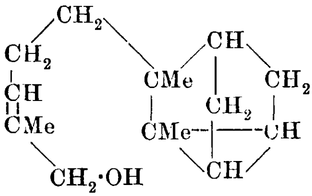
$$\begin{array}{l}NH_2\cdot CMe{-}CO \\ \qquad\; | \\ \quad\;\; CH_2\cdot CH_2\end{array}\!\!>CHPr^{\beta},$$

b. p. 68°/18 mm. or 173°/760 mm., which has a strong odour and rapidly absorbs carbon dioxide, forming a snow-white mass. The corresponding *carbamide*, $C_9H_{17}\cdot NH\cdot CO\cdot NH_2$, m. p. 129—130°, crystallises in slender needles from acetic acid. T. A. H.

Constituents of Ethereal Oils. Further Degradation of Noreksantalic Acid. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1910, **43**, 1890—1892. Compare this vol., i, 495, and following abstract).—Methyl noreksantalate is converted by sodium and alcohol into *noreksantalol*, $C_{11}H_{18}O$, b. p. 114—117°/10 mm., D^{20} 0·9958, n_D 1·49049, α_D −0·7° (100 mm. tube), a benzene solution of which is oxidised by potassium dichromate and dilute sulphuric acid to *noreksantalal*, $C_{11}H_{16}O$, b. p. 92—94°/11 mm., D^{20} 0·9964, n_D 1·48301, α_D −30·8° (100 mm. tube), the *semicarbazone* of which has m. p. 224°. The CHO group of the aldehyde must be attached to a methylene group, because enol-*noreksantalal acetate*, $C_{11}H_{15}\cdot OAc$, b. p. 110—113°/10 mm., D^{20} 1·0270, n_D 1·48374, α_D −25·6° (100 mm. tube), obtained from the aldehyde, acetic anhydride, and sodium acetate, is oxidised in acetone solution by potassium permanganate to teresantalic acid, $C_{10}H_{14}O_2$. The formation of this acid, which contains 10 atoms of carbon, is another proof that the compounds of the noreksantalic acid series contain 11 atoms of carbon; numbers of the eksantalic acid series contain 12 atoms of carbon. In all three series occurs the same tricyclic system as is present in α-santalol. C. S.

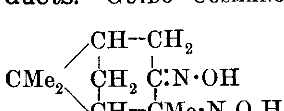
Constituents of Ethereal Oils. Constitutions of the α-Santalol and of the α-Santalene Series, and of Sesquiterpene Alcohols and of Sesquiterpenes. FRIEDRICH W. SEMMLER (*Ber.*, 1910, **43**, 1893—1898).—"Santalol," obtained by distilling oil of sandel-wood with steam, converting the oil in the distillate into the hydrogen phthalate, and hydrolysing the ester, is a mixture of two

primary alcohols: $C_{15}H_{24}O$, which can be tolerably satisfactorily separated by repeated fractionation into α-santalol, b. p. 159—160°/10 mm., D^{20} 0·978, n_D 1·498, α_D 1° (100 mm. tube), and β-santalol, b. p. 167—168°/10 mm., D^{20} 0·9715, n_D 1·509, α_D −42° (100 mm. tube). The molecular refraction of the "santalol," regenerated from the hydrogen phthalates, indicates the presence therein of a singly unsaturated tricyclic alcohol and a doubly unsaturated dicyclic alcohol. The assumption that the former is α-santalol and the latter β-santalol is justified by the results of oxidising "santalol." Oxidation by potassium permanganate gives tricyclic eksantalic acid, $C_{12}H_{18}O_2$, and oxidation by ozone gives tricyclic eksantalal, $C_{12}H_{18}O$; the yields of the acid and of the aldehyde are best in the lower-boiling fractions, that is, those rich in α-santalol. Eksantalal has been converted into teresantalic acid (preceding abstract), the constitution of which is known. The author gives reasons for assigning to teresantalic acid a constitution based on the camphor type, not on the camphene type. Consequently, eksantalal, eksantalic acid, and therefore the sesquiterpene alcohol, α-santalol, have constitutions based on the camphor type. The last-mentioned alcohol has the annexed constitution.

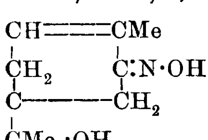


C. S.

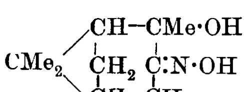
α-Pinene*iso*nitroamineoxime and Its Decomposition Products. Guido Cusmano (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 747—753. Compare this vol., i, 182).—Nitrous acid reacts with the hydroxylamino-group of α-pinenehydroxylamineoxime, forming the *iso*nitroamineoxime, I, which is fairly stable when dry. When suspended in water and heated on the water-bath, however, it is converted into hydroxydihydrocarvoxime, II (compare Wallach, Abstr., 1896, i, 571), and nitrous oxide. A similar decomposition is effected by dilute acetic acid. Alkalis act differently, however, for they yield nitrous acid, nitrosopinene, and hydroxypinocamphoneoxime, III (the oxime of pinene hydrate). A substance, m. p. 70—80°, is also formed, but it is not crystalline. Since pinene*iso*nitroamineoxime yields hyponitrous acid (or nitrous oxide and water), however, it may be decomposed; it appears that the substance reacts as though it had the formula IV (compare this vol., i, 182).



(I.)



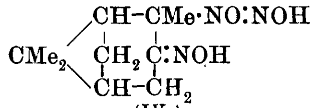
(II.)



(III.)

α-Pinene*iso*nitroamineoxime is obtained by the action of an aqueous solution of sodium nitrite on an aqueous solution of the hydrochloride or sulphate of pinene-*o*-hydroxylamineoxime; it forms large, colourless prisms, m. p. 127° (decomp.), dissolves in alkali carbonates, gives Liebermann's reaction, and a wine-red coloration

with ferric chloride. The *sodium* salt, prepared with the aid of sodium ethoxide, decomposes at 92—95°. The *hydroxylamine* salt,



(IV.)

$C_{10}H_{17}O_2N_2\cdot NH_2\cdot OH$,

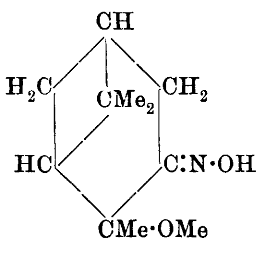
crystallises in lustrous prisms, m. p. 110° (decomp.); it reduces Fehling's solution in the cold, and barely shows Liebermann's reaction. o-*Hydroxypinocamphoneoxime*, which is best obtained (yield 20%) by the slow decomposition of the sodium salt of the *iso*nitroamine at the ordinary temperature, crystallises in lustrous, rhombic prisms, m. p. 128° (softening a few degrees previously). The substance resists prolonged boiling with aqueous or alcoholic solutions of alkaline hydroxides, but it is at once attacked by acids. When treated with hydrochloric acid, even in the cold, it loses its oximic group. Dilute acetic acid does not affect the oximic group, but converts the compound completely into hydroxydihydrocarvoxime.

R. V. S.

Sesquiterpenes. IV. ERNST DEUSSEN [with HANS PHILIPP] (*Annalen*, 1910, **374**, 105—120. Compare Abstr., 1909, i, 813).—A. *Gurjun balsam oil*.—This oil varies considerably in composition, and contains at least two distinct sesquiterpenes, named provisionally, α- and β-gurjunene. α-*Gurjunene* is a strongly lævorotatory oil, b. p. about 119°/12 mm., and is probably a dicyclic sesquiterpene. β-*Gurjunene* is a slightly dextrorotatory oil, b. p. about 122·5—123·5°/12 mm., and is probably a tricyclic compound. Both sesquiterpenes, when oxidised by potassium permanganate, yield a *ketone*, $C_{15}H_{24}O$, a colourless oil, b. p. 175—178°/12 mm., α_D +120—130°, D 1·0160, n_D 1·5303; the *oxime* of the ketone is pale yellow, and has b. p. 204°/12 mm. Gurjun balsam oil, when treated with hydrogen chloride and subsequently with anhydrous sodium acetate and glacial acetic acid, yields iso*gurjunene*, a dicyclic sesquiterpene, b. p. 129·5—132°/12 mm., which when oxidised does not yield a ketone forming a crystalline semicarbazone.

B. "*Caryophyllene*."—The substance m. p. 125—125·5°, which was isolated from the mother liquor obtained in the preparation of α-caryophyllene nitrosochloride (*loc. cit.*), is shown to be a *nitrosoethoxycaryophyllene*, $OEt\cdot C_{15}H_{24}\cdot NO$.

Monoterpenes.—I. The substance obtained by the action of sodium methoxide on pinene nitrosochloride (*loc. cit.*) is *oximinomethoxyhydropinene* (annexed formula). It is converted (1) by phenyl carbimide into the corresponding *urethane*,



$OMe\cdot C_{10}H_{15}\cdot NO\cdot CO\cdot NHPh$,

which crystallises in rosettes of needles, m. p. 102°, and (2) by an alcoholic solution of hydrogen chloride into *i*-chlorohydrocarvoxime.

Nitrosopinene, when treated with phenylcarbimide, yields the corresponding *urethane*, $C_{17}H_{20}O_2N_2$, m. p. 101—102°.

II. Pinene nitrosochloride as usually prepared, when washed with ethyl alcohol, yields a dextrorotatory solution in chloroform, and when treated with benzylamine yields a nitrolbenzylamine, together with a *substance* (pinenenitrolbenzylamine?) which crystallises in needles, m. p. 148—149°, $[\alpha]_D$ +96·7° (1·191% solution in ethyl acetate). The presence of an oximino-group in pinenenitrolbenzylamine is demonstrated by the formation of a *urethane*,

$$CH_2Ph\cdot NH\cdot C_{10}H_{15}\colon NO\cdot CO\cdot NHPh,$$

m. p. 189·5—190° (decomp.), when it is treated with phenylcarbimide.

W. H. G.

Scutellarin. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Monatsh.*, 1910, 31, 439—491. Compare Goldschmiedt and Molisch, Abstr., 1902, i, 48).—An amplification of work already recorded. The formula $C_{21}H_{20}O_{12}$, previously attributed to scutellarin, is altered to $C_{21}H_{18}O_{12}$, as a consequence of further analysis and of its hydrolysis to scutellarein and glycuronic acid. Scutellarin is shown to be homogeneous by extraction with methyl alcohol, whereby only a slight black powder, chiefly inorganic, remains; the substance in the alcoholic solution is fractionally crystallised, yielding fractions having practically the same properties. The colour reaction with α-naphthol and sulphuric acid is shown to be characteristic of glycuronic acid. By titration with *N*/10-potassium hydroxide and phenolphthalein, by estimating the carbon dioxide liberated from barium carbonate by scutellarin, and by the analysis of the barium salt, scutellarin is proved to contain one carboxyl and one phenolic hydroxyl group. The acetate, m. p. 263—265° (decomp.), contains five acetyl groups, and regenerates scutellarin by hydrolysis. When oxygen is passed for four days into a solution of scutellarin in 25% potassium hydroxide, the ethereal extract of the resulting solution contains *p*-hydroxyacetophenone.

The hydrolysis of scutellarin is best effected by adding concentrated sulphuric acid to a rapidly stirred suspension of finely powdered scutellarin in water until solution is complete, and then pouring the mixture into cold water. The operation requires only thirty to forty seconds, a quantitative precipitate of scutellarein is obtained, and the filtrate contains glycuronic acid.

Scutellarein, $C_{15}H_{10}O_6$, is undoubtedly a flavone derivative by reason of its behaviour as a mordant dye, its property of forming salts with metals or acids, and the nature of its products of decomposition by alkalis. It is oxidised by boiling 14—15% nitric acid to picric, oxalic, and 3:5-dinitro-4-hydroxybenzoic acids. By acetylation it yields a *tetra-acetate*, $C_{15}H_6O_6(OAc)_4$, m. p. 235—237°.

Methylation by ethereal diazomethane yields *scutellarein trimethyl ether*, $C_{15}H_7O_3(OMe)_3$, m. p. 189—190°, whilst the action of methyl iodide and methyl-alcoholic potassium hydroxide results in the formation of the trimethyl ether, together with a small amount of a *tetramethyl ether*, m. p. 158—160°.

The hydrolysis of scutellarein by boiling 12% potassium hydroxide or by fusion with potassium hydroxide yields *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid, and a substance which gives the pine-shaving reaction of phloroglucinol.

The preceding results are explained by regarding scutellarein as 1 : 3 : 4 : 4′-(or 1 : 2 : 3 : 4′-)tetrahydroxyflavone, and scutellarin provisionally as $R\cdot O\cdot \underbrace{CH\cdot[CH\cdot OH]_2\cdot CH}_{O}\cdot CH(OH)\cdot CO_2H$, where R represents the scutellarein residue. C. S.

Cornin, the Bitter Principle of Cornus Florida. EMERSON R. MILLER (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, **7**, xlii—xliii).—The best yields are obtained from the root-bark. It crystallises in colourless, silky needles or rectangular plates, m. p. 181°, and has neither basic nor acidic properties. Its aqueous solutions do not yield precipitates with silver nitrate or lead subacetate, but when kept for some time they reduce Fehling's solution, and when heated with a little alkali reduce Fehling's solution immediately. The aqueous solution also gives Pettenkofer's test for dextrose. It appears to be a glucoside with the composition represented by the formula $C_{17}H_{24}O_{10}$ or $C_{16}H_{21}O_9\cdot OMe$. J. J. S.

Action of Phosphorus Pentachloride on Picrotin. PAUL HORRMANN (*Ber.*, 1910, **43**, 1903—1907).—Phosphorus pentachloride acts as a dehydrating agent on picrotin in boiling chloroform, converting it into *anhydropicrotin*, $C_{15}H_{16}O_6$, m. p. 317° (decomp.), which does not reduce Fehling's solution or ammoniacal silver oxide solution, forms a *benzoate*, $C_{22}H_{20}O_7$, m. p. 250°, an *acetate*, $C_{17}H_{18}O_7$, m. p. 237°, and a *diacetate*, $C_{19}H_{20}O_8$, m. p. 192·5°, and dissolves in hot *N*/10-sodium hydroxide, the solution after acidification yielding *anhydropicrotinic acid*, $C_{15}H_{18}O_7,H_2O$, which decomposes at 221°, or in the anhydrous state at 233°.

The chloroform mother liquor contains a halogenated substance, which by prolonged boiling with methyl alcohol is converted into a *substance*, $C_{16}H_{21}O_8P$, m. p. 211°, which has not been further examined. C. S.

Picrotoxin. FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 473—480. Compare this vol., i, 404). The reduction of α-picrotinic acid with hydriodic acid and red phosphorus yields, not only the acid, $C_{15}H_{18}O_4$, previously described (*loc. cit.*), but also a *ketone*, which from the composition of its *oxime* should have the formula $C_{14}H_{16}O_3$. When picrotoxin is heated with hydrochloric acid (of D 1·19, diluted with an equal volume of water) in a sealed tube for five hours at 170—180°, it also gives a *ketone*, $C_{14}H_{15}ClO_3$, which results from the substitution of an hydroxyl group by chlorine and loss of carbon dioxide. Picrotin yields the same substance, losing at the same time the molecule of water by which its formula differs from that of picrotoxin, so that both substances must contain the same nucleus. The ketone crystallises in small needles, m. p. 114—115°; it is insoluble in alkalis, and it forms an osazone, m. p. 196°, which does not contain halogen.

In order to obtain an indication of the presence of an aromatic nucleus, which from other reasons is probable, picrotinic acid, $C_{15}H_{18}O_4$, was nitrated with a mixture of equal volumes of concentrated

sulphuric acid and nitric acid (D 1·48) A *nitro*-derivative, $C_{18}H_{15}O_6N$, was obtained; it crystallises in pale yellow needles, m. p. 166°, and is very stable towards oxidising agents. A small quantity of a *substance* insoluble in alkali was also formed; it had m. p. about 110°. When the above nitro-derivative was reduced with ammonium sulphide, another *nitro*-compound was formed, m. p. 173° (previously softening).

R. V. S.

Method of Preparing Dimethylpyrone. ZDENKO H. SKRAUP and J. PRIGLINGER (*Monatsh.*, 1910, **31**, 363—369).—A mixture of 95 grams of acetic anhydride and 20 c.c. of sulphuric acid is boiled for four hours, and distilled as completely as possible in a vacuum. The solution of the residue in saturated ammonium sulphate is faintly basified by ammonium hydroxide, filtered, and repeatedly extracted with benzene. The extracts contain about 4 grams of 2 : 6-dimethylpyrone, m. p. 132—133°. It is shown that the pyrone does not exist as such in the acetic anhydride.

In still poorer yield dimethylpyrone is obtained by heating acetic anhydride with phosphoric oxide, or by heating a mixture of acetyl chloride, glacial acetic acid, and sulphuric acid.

Dimethylpyrone is easily converted into lutidone by dissolving it in a little water, saturating the solution with ammonia, and heating the mixture in a sealed tube for eight hours in a water-bath. C. S.

Synthesis of 2 : 3-Dihydroxyflavone. J. REIGRODSKI and JOSEF TAMBOR (*Ber.*, 1910, **43**, 1964—1968).—Hydroxyquinol trimethyl ether reacts with acetyl chloride in the presence of aluminium chloride and carbon disulphide, yielding 2 : 4 : 5-*trimethoxyacetophenone*, $C_6H_2(OMe_3)\cdot COMe$, which crystallises from alcohol in small, colourless needles, m. p. 102—103°. The ketone reacts with methyl benzoate and sodium (granulated) at 115—120°, yielding 2 : 4 : 5-*trimethoxybenzoylacetophenone*, $COPh\cdot CH_2\cdot CO\cdot C_6H_2(OMe)_3$, which crystallises in small, ochre-yellow prisms, m. p. 105°. It gives a dark green coloration with ferric chloride, and when boiled for four hours with concentrated hydriodic acid yields 2 : 3-*dihydroxyflavone*, $C_6H_2(OH)_2{<}\begin{matrix}O-CPh\\ \quad\ \ \|\\ CO\cdot CH\end{matrix}$, which crystallises from dilute alcohol in colourless, microscopic prisms containing $1H_2O$, and with m. p. 135° (decomp.). Its *diacetyl* derivative, $C_{19}H_{14}O_6$, crystallises in thin needles, m. p. 195°, and its *dimethyl ether*, $C_{17}H_{14}O_4$, in slender, colourless needles, m. p. 189°.

2 : 4 : 5-Trimethoxyacetophenone condenses with aldehydes, yielding chalkone derivatives (Abstr., 1904, i, 426). With benzaldehyde it yields 2 : 4 : 5-*trimethoxychalkone*, $C_6H_2(OMe)_3\cdot CO\cdot CH\!:\!CHPh$, which crystallises in canary-yellow needles, m. p. 113—114°. Its solution in concentrated sulphuric acid is orange-coloured, and its *dibromide*, $C_{18}H_{18}O_4Br_2$, crystallises in pale yellow, prismatic plates, m. p. 148° (decomp.).

2-*Hydroxy*-2′ : 4′ : 5′-*trimethoxybenzylideneacetophenone* (2-*hydroxy*-2′ : 4′ : 5′-*trimethoxychalkone*), $OH\cdot C_6H_4\cdot CH\!:\!CH\cdot CO\cdot C_6H_2(OMe)_3$, obtained by condensing salicylaldehyde with trimethoxyacetophenone

and alkali, crystallises in green needles, m. p. 159—160° (decomp.). The *acetyl* derivative, $C_{20}H_{20}O_6$, crystallises in glistening, golden needles, and the *acetyl-dibromide*, $C_{20}H_{20}O_6Br_2$, forms colourless needles, m. p. 132° (decomp.). The latter compound reacts with alcohol and concentrated potassium hydroxide solution, yielding 2′ : 4′ : 5′-*trimethoxy*-1-*benzoylcoumarone*, $C_6H_4<{O \atop CH}>C\cdot CO\cdot C_6H_2(OMe)_3$, which crystallises from dilute alcohol in prismatic, yellow needles, m. p. 125°. Its solution in concentrated sulphuric acid is orange-coloured.

J. J. S.

1 : 3-Dimethoxycoumaranone. H. DUMONT and JOSEF TAMBOR (*Ber.*, 1910, **43**, 1969—1971).—*a-Bromophloroacetophenone trimethyl ether* (1 : 3 : 5-*trimethoxy*-1-*bromoacetylbenzene*), $C_6H_2(OMe)_3\cdot CO\cdot CH_2Br$, obtained by the Friedel-Crafts synthesis from bromoacetyl bromide and phloroglucinol trimethyl ether, crystallises in colourless needles, m. p. 126°, and when boiled with alcoholic potassium acetate (compare Blom and Tambor, Abstr., 1905, i, 916) yields 1 : 3-dimethoxycoumaranone, $C_6H_2(OMe)_2<{O \atop CO}>CH_2$, which is identical with Friedländer and Schnell's dimethoxyketocoumaran (Abstr., 1898, i, 24).

1 : 3 : 2′ : 3′-*Tetramethoxybenzylidenecoumaranone*,

$$C_6H_2(OMe)_2<{O \atop CO}>C:CH\cdot C_6H_3(OMe)_2,$$

obtained by condensing 1 : 3-dimethoxycoumaranone with *o*-veratraldehyde and alkali, crystallises in yellow needles, m. p. 166°. Its solution in concentrated sulphuric acid is dark orange-coloured.

The isomeric 1 : 3 : 2′ : 4′-*tetramethoxy*-compound, obtained from 1 : 3-dimethoxycoumaranone and 2 : 4-dimethoxybenzaldehyde, forms yellow needles, m. p. 209°; its solution in concentrated sulphuric acid is blood-red. The 1 : 3 : 3′ : 4′-*tetramethoxy*-derivative has m. p. 175°, and also yields a blood-red solution in sulphuric acid. J. J. S.

Sulphur Derivatives of Ethyl Chlorocyanoacetoacetate. ERICH BENARY (*Ber.*, 1910, **43**, 1943—1956. Compare Abstr., 1908, i, 600).—Ethyl γ-chloro-α-cyanoacetoacetate reacts with an aqueous 15% solution of potassium hydrogen sulphide, yielding crystals of ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate,

$$S<{CH_2 \text{———} CO \atop C(:NH)\cdot CH\cdot CO_2Et},$$

and ethyl thiobiscyanoacetoacetate, $S[CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et]_2$, which remains dissolved in the alkaline solution, and is precipitated on the addition of dilute sulphuric acid.

Ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate crystallises in flat, silvery needles, m. p. 219—220° (decomp.), after turning brown at 200°. It dissolves in dilute sodium hydroxide solution, but is rapidly decomposed. The *diacetyl* derivative, $C_{11}H_{13}O_5NS$, crystallises in hard lamellæ, m. p. 108—109°. When the ester is dissolved in 10% sodium hydroxide solution, and kept for twenty-four hours, it

yields 3-*cyano*-2 : 4-*diketotetrahydrothiophen*, $S<\begin{array}{l}CH_2\cdot C\cdot OH\\ CO—C\cdot CN\end{array}$, which is probably formed by the rupture of the sulphur ring and its subsequent closing by the elimination of ethyl alcohol. The product crystallises with $1H_2O$, has m. p. 181—182° (decomp.), is a monobasic acid, and hence has the keto-enolic constitution. The *silver* salt, $C_5H_2O_2NSAg$, is sparingly soluble, and the acid, which dissolves readily in most solvents, is best purified by conversion into its *diacetyl* derivative, $C_9H_7O_4NS$, which forms colourless needles, m. p. 63—64°. 3-*Cyano*-2 : 4-*diketo*-5-*benzylidenetetrahydrothiophen*,

$$CHPh:C<\begin{array}{l}C(OH):C\cdot CN\\ S——CO\end{array},$$

obtained by condensing the ketone with benzaldehyde in the presence of sodium ethoxide, crystallises in pale yellow needles, m. p. 220° (decomp.), and forms a *sodium* salt, $C_{12}H_6O_2NSNa$, which separates as colourless crystals from alcohol. When boiled with excess of barium hydroxide solution for half an hour, the nitrile yields the bimolecular *compound*, $C_{20}H_{12}O_8N_4S_4$, as colourless needles, m. p. 198° (decomp.), after turning brown at 180°. It is sparingly soluble in water, and yields a *barium* salt, $(C_{20}H_5O_4N_2S_2)_2Ba$, as a colourless syrup which sets to a vitreous mass. When heated on the water-bath for a quarter of an hour with five times its weight of concentrated sulphuric acid, the nitrile takes up water and yields 2 : 4-*diketotetrahydrothiophen*-3-*carboxylamide*, $S<\begin{array}{l}CH_2\cdot C\cdot OH\\ CO—C\cdot CO\cdot NH_2\end{array}$, which is deposited when the mixture is poured onto ice as a sparingly soluble, crystalline powder, m. p. 177—178° (decomp.). It yields a *potassium* salt, $C_5H_4O_3NSK$, which is sparingly soluble in alcohol. It has not been found possible to transform the nitrile or amide into the corresponding acid.

2-*Imino*-4-*ketotetrahydrothiophen*, $S<\begin{array}{l}CH_2——C\cdot OH\\ C(:NH)\cdot CH\end{array}$, obtained by heating the ketonic ester with twenty times its weight of fuming hydrochloric acid, crystallises from water in colourless needles, which turn brown at 190°, and decompose at 215°. Its aqueous solution is neutral, but it dissolves in both alkalis and dilute acids. With a chloroform solution of bromine, it yields the 3-*bromo*-derivative, $S<\begin{array}{l}CH_2——C\cdot OH\\ C(:NH)\cdot CBr\end{array}$, which crystallises in brownish-coloured needles, m. p. 157°, and yields a *hydrobromide*. With nitrous acid it yields the 3-*oximino*-derivative, $S<\begin{array}{l}CH_2——CO\\ C(:NH)\cdot C:N\cdot OH\end{array}$, as violet needles, decomposing at 175°, and when this is reduced with zinc dust and acetic acid, 3-*amino*-2-*imino*-4-*ketotetrahydrothiophen*, $S<\begin{array}{l}CH_2——C\cdot OH\\ C(:NH)\cdot C\cdot NH_2\end{array}$, is obtained as plates, which turn brown at 140°, and are completely decomposed at 174—175°. The *benzylidene* derivative of the amine, $C_{11}H_{10}ON_2S$, decomposes at 181°. The amine reacts with nitrous acid, yielding an *acid*, $C_4H_5O_2N_3S$, which decomposes at 200°, and forms a *lead* salt as a brown precipitate.

The imino-ketone reacts with warm formaldehyde solution, yielding *methylenebis-4-keto-2-iminotetrahydrothiophen*,

$$CH_2\left[C<\begin{matrix}C(OH)\text{—}CH_2\\ \qquad\qquad | \\ C(:NH)\cdot S\end{matrix}\right]_2,$$

as colourless, soft, felted needles, which darken at 260°.

Ethyl thiobiscyanoacetoacetate crystallises from alcohol in glistening plates, m. p. 98—99°, and is the only product formed when hydrogen sulphide is passed into an alkaline solution of ethyl chlorocyanoaceto-acetate. It yields a green precipitate with cupric acetate, is not hydrolysed by cold alkalis, but with concentrated sulphuric acid yields ethyl 2-iminc-4-ketotetrahydrothiophen-3-carboxylate and *a-carboxylamido-tetronic acid*, $O<\begin{matrix}CH_2\cdot C\cdot OH\\ \|\\ CO\text{—}C\cdot CO\cdot NH_2\end{matrix}$, as colourless needles, m. p. 182—183° (decomp.).

Ethyl a-cyano-γ-thiocyanoacetoacetate,

$$NCS\cdot CH_2\cdot C(OH):C(CN)\cdot CO_2Et,$$

obtained by the action of potassium thiocyanate on an alkaline solution of ethyl chlorocyanoacetoacetate, crystallises in slender needles, m. p. 82—84°. It decomposes when left exposed to the air, and when left in contact with fuming hydrochloric acid for twenty-four hours yields ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate, but with cold concentrated sulphuric acid, it yields *ethyl a-cyano-γ-thiocarbamatoacetoacetate*, $NH_2\cdot CO\cdot S\cdot CH_2\cdot C(OH):C(CN)\cdot CO_2Et$, as soft needles, m. p. 155—156°.

Practically all the compounds with the exception of the original 2-imino-4-ketotetrahydrothiophencarboxylate give deep red colorations with ferric chloride, and exist in the enolic forms given above.

J. J. S.

Rotatory Power of Normal Quinine Hydrochloride. André and Leulier (*J. Pharm. Chim.*, 1910, [vii], 2, 22).—Experiments show that the specific rotatory power of normal quinine hydrochloride increases with the dilution, whereas the French Codex states diametrically the opposite, namely, that it increases with the concentration of the solution.

L. de K.

Action of Chlorine and Ammonia on Quinine. Ezio Comanducci (Pamphlet 12 pp.).—By the action of chlorine or other oxidising agents followed by ammonia on salts of quinine, a number of coloured compounds are produced. In addition to the thalleioquinine ($C_{15}H_{20}O_5N_2$), erythroquinine, rusioquinine ($C_{24}H_{60}O_{16}N_3$), melanoquinine ($C_{26}H_{36}O_{12}N_3$), and a colourless derivative previously known, the author has obtained a reddish-violet compound, rubroquinine, and a colourless substance, leucoquinine. From an examination of numerous quinine derivatives containing a phenolic hydroxyl group, the author comes to the conclusion that the production of these coloured substances depends on the presence of a phenolic group attached to a naphthalene or quinoline nucleus. Thalleioquinine is obtained as a green precipitate, m. p. 130°, by treating a quinine solution with chlorine water, and adding ammonia a few seconds

afterwards. On further treatment with chlorine water and ammonia, it yields a red *substance*, which contains chlorine. When the addition of ammonia is delayed about three times as long as in the case of thalleioquinine, and the ammonia added in two portions, *rubroquinine* is precipitated; it has m. p. 118—120°, is soluble in chlorine water, and is reprecipitated on adding ammonia. When a solution of quinine sulphate is treated with chlorine water for five minutes and then quickly with ammonia, a white precipitate, *leucoquinine*, is obtained. It has m. p. 138°, and is slightly soluble in chlorine water; on adding ammonia to the solution, a red precipitate is obtained. Rubroquinine and leucoquinine are soluble in acids.

R. V. S.

Constitution of Cinchonicine (Cinchotoxine). II. Derivatives and Salts of Ethyl-, Phenyl-, and α-Naphthyl-cincotoxol. EZIO COMANDUCCI (*Rend. R. Accad. Sci. Fis. Mat. Napoli*, 1910, Reprint 11 pp. Compare Abstr., 1909, i, 409).—By the preparation of the derivatives described in this paper, it is established that the vinyl group, and secondary and tertiary nitrogen atoms of cinchonicine are present also in the cinchotoxoles, whilst the ketonic group has been converted into a tertiary alcoholic grouping.

Ethyl cinchotoxol hydrochloride, $C_{21}H_{28}ON_2,2HCl$, has m. p. 108—109° (sintering at 100°), and $[\alpha]_D^{15}$ +51·75°. The *platinichloride*, $C_{21}H_{28}ON_2,H_2PtCl_6,H_2O$, is a red, crystalline powder, m. p. 210°. The *aurichloride*, $C_{21}H_{28}ON_2,2HAuCl_4,3H_2O$, a yellow, crystalline powder, has m. p. 120—121°. The *picrate*,

$$C_{21}H_{28}ON_2,2C_6H_3O_7N_3$$

is prepared from the hydrochloride; it is a yellow powder, which sinters at 80°, and has m. p. 102°. When an insufficient quantity of picric acid is taken, a *picrate hydrochloride*, $C_{21}H_{28}ON_2,HCl,C_6H_3O_7N_3$, m. p. 98°, is obtained. The *tartrate*, $C_{21}H_{28}ON_2,C_4H_6O_6,H_2O$, sinters at 95°, and melts at 107° (decomp.). The *methiodide*, $C_{21}H_{28}ON_2,MeI$, forms small, reddish-brown crystals, m. p. 138—140°. The *nitroso*-derivative, $C_{21}H_{27}ON_2{\cdot}NO$, has m. p. 147—150° (decomp.); it gives Liebermann's reaction. The *benzoyl* derivative, $C_{21}H_{27}ON_2{\cdot}COPh$, forms white, crystalline scales, m. p. 114°. The *bromine* derivative, $C_{21}H_{28}ON_2Br_2$, is obtained by mixing chloroform solutions of bromine and the base; it is a reddish-white powder, m. p. 190° (sintering at 150°).

Phenylcinchotoxol hydrochloride, $C_{18}H_{22}N_2{:}CPh{\cdot}OH,2HCl$, sinters at 75°, and melts at 86—100°; it has $[\alpha]_D^{15}$ +21·09°. The *platinichloride*, $C_{25}H_{28}ON_2,H_2PtCl_6,H_2O$, is a yellow powder, which decomposes above 200°. The *aurichloride*, $C_{25}H_{28}ON_2,2HAuCl_4$, forms yellow tablets, which sinter at 70°, and melt at 113—115°. The *picrate*,

$$C_{25}H_{28}ON_2,C_6H_3O_7N_3,$$

is a yellow powder, m. p. 105°. The *tartrate*,

$$C_{25}H_{28}ON_2,C_4H_6O_6,3\tfrac{1}{2}H_2O,$$

forms tablets or prisms, m. p. 225° (becoming brown at 180°); the anhydrous substance has m. p. 240°. The *methiodide*, $C_{25}H_{28}ON_2,MeI$, has m. p. 127—129° (sintering at 120°). The *nitroso*-derivative, $C_{25}H_{27}ON_2{\cdot}NO,HCl$, has m. p. 147—149°, and decomposes at 150°; it

gives Liebermann's reaction. The *bromo*-derivative, $C_{25}H_{28}ON_2Br_2$, sinters at 150° and melts at 195°. The *benzoyl* derivative,

$$C_{25}H_{27}ON_2 \cdot COPh,$$

forms red scales, which sinter at 165°, and melt at 178° (decomp.). When phenylcinchotoxole is treated with a 2% solution of potassium permanganate at 2°, formic acid is produced, in addition to a yellow, crystalline *substance* of slightly acid reaction, which has m. p. 188° (becoming brown at 167°).

a-Naphthylcinchotoxol hydrochloride, $C_{18}H_{22}N_2{:}C(C_{10}H_7)\cdot OH,2HCl$, is a deliquescent, reddish-brown mass, m. p. 71—85° (sintering at 60°); it has $[a]_D^{15}$ +49·6°. The *platinichloride*, $C_{29}H_{30}ON_2,H_2PtCl_6,H_2O$, forms a yellow, amorphous powder, which becomes brown, and decomposes at 330°. The *aurichloride*, $C_{29}H_{30}ON_2,2HAuCl_4,H_2O$, is a yellow powder, m. p. 144—145° (decomp.). The *picrate hydrochloride*,

$$C_{29}H_{30}ON_2,C_6H_3O_7N_3,HCl,$$

sinters at 97°, and has m. p. 101° (decomp.). The *methiodide*,

$$C_{29}H_{30}ON_2,MeI,$$

is a reddish-brown substance, m. p. 140°. R. V. S.

Constitution of Cinchonicine (Cinchotoxine). III. Chloroethyl- and Chlorophenyl-cinchotoxile. EZIO COMANDUCCI (*Rend. R. Accad. Sci. Fis. Mat. Napoli*, 1910, Reprint 5 pp. Compare preceding abstract).—By the action of phosphoryl chloride and phosphorus pentachloride in chloroform solution, the alcoholic hydroxyl group of the *R*-cinchotoxols (compare Abstr., 1909, i, 409) may be replaced by chlorine; the substances so obtained are termed by the author chloro-*R*-cinchotoxiles.

Chloroethylcinchotoxile, $C_{18}H_{21}N_2{:}CEtCl$, is a reddish-brown powder, which sinters at 85°, and melts at 115—117°. The *platinichloride*, $C_{21}H_{26}N_2Cl,H_2PtCl_6$, forms a reddish-yellow powder, which becomes brown at 210°. The *picrate*, $C_{21}H_{26}N_2Cl,C_6H_3O_7N_3$, is a yellow powder, which becomes brown at 115°, and melts at 130°.

Chlorophenylcinchotoxile forms dark yellow scales, m. p. 148—155°. The *platinichloride*, $C_{25}H_{26}N_2Cl,H_2PtCl_6$, becomes brown, and decomposes at 220°. The *picrate*, $C_{25}H_{26}N_2Cl,C_6H_3O_7N_3$, has m. p. 121—122°. By the action of alcoholic potassium hydroxide on the chlorophenyl-derivative, a *compound* was obtained, which had m. p. 62—63°, and was free from chlorine. R. V. S.

Strychnine and Brucine. ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 555—561. Compare Beckurts, Abstr., 1905, i, 918, and Martin, Abstr., 1904, i, 446).—By the action of bromine on a solution of strychnine in glacial acetic acid, a *dibromide*, $C_{21}H_{22}O_2N_2Br_2$, is produced. The substance crystallises from alcohol in rosettes of colourless needles, m. p. 122°, but by repeated crystallisation from alcohol, or by heating above its m. p., it is converted into another, more stable form, which forms large, colourless, monoclinic crystals, m. p. 260°. In the preparation of the dibromide the formation of a *perbromide*, $C_{21}H_{22}O_2N_2Br_3$, may occur. When the dibromide is boiled with water, it dissolves, and the solution on cooling

deposits the *hydrobromide* of the monobromostrychnine, m. p. 222°, of Beckurts (*loc. cit.*) and Martin (*loc. cit.*). This monobromostrychnine does not lose bromine even when heated with alcoholic potassium hydroxide in a sealed tube. With chloroanil in ethereal-alcoholic solution it gives a violet coloration, and with concentrated sulphuric acid and potassium dichromate it yields a fugitive, reddish-violet coloration. When it is treated with bromine, a *perbromide*, $C_{21}H_{22}O_2N_2Br_6,H_2O$, is formed, which crystallises in golden-yellow needles, which on heating darken at 200° with loss of bromine. On heating this compound with water or with thiosulphate solution, a *substance* is obtained containing 28·35—28·49% bromine. From the methyl-alcoholic mother liquors of the perbromide, a crystalline *hydrobromide* of the composition $C_{21}H_{21}O_2N_2Br,Br_2,HBr,H_2O$ can be obtained. From the mother liquor of this substance the addition of potassium hydroxide precipitates the *dibromide* of monobromostrychnine; it could not be crystallised.

Whilst strychnine and monobromostrychnine reduce acid solutions of permanganate at once, the dibromides of these substances only do so after a time. Monobromostrychnine and the two dibromides do not react with hydroxylamine or with *p*-nitrophenylhydrazine. The authors consider that the above behaviour may be explained by the presence of the grouping $X\lessgtr\begin{matrix}CH\\ \|\\ C\end{matrix}$ in strychnine, the constitutions of the above derivatives being represented by the following formulæ:

$$C_{19}H_{21}O_2N_2\lessgtr\begin{matrix}CHBr\\ |\\ CBr\end{matrix}, \quad C_{19}H_{21}O_2N_2\lessgtr\begin{matrix}CBr\\ \|\\ C\end{matrix},HBr,$$

$$C_{19}H_{21}O_2N_2\lessgtr\begin{matrix}CBr\\ \|\\ C\end{matrix}, \quad C_{19}H_{21}O_2N_2\lessgtr\begin{matrix}CBr_2\\ |\\ CBr\end{matrix}.$$

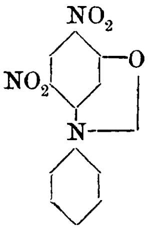
R. V. S.

Amine Peroxides of Brucine and Strychnine. GUSTAV MOSSLER (*Monatsh.*, 1910, 31, 329—345).—When brucine is heated with 3% hydrogen peroxide on the water-bath and the solution is concentrated in a vacuum, crystals of a *peroxide* containing two atoms of active oxygen are obtained, which contain $4H_2O$ when slowly crystallised, $3H_2O$ when rapidly crystallised, and $2H_2O$ when dried in a vacuum. Another mol. of H_2O can be expelled at 100° or by crystallisation from alcohol, but the elimination of the remaining H_2O is accompanied by the loss of the active oxygen. The peroxide has m. p. 202—203° (decomp.), the air-dried crystals softening at 115—125°, those dried in a vacuum at 135°. In aqueous solution the peroxide dissociates into brucine oxide and hydrogen peroxide, but it dissolves without decomposition in non-dissociating solvents, alcohol, or chloroform. An aqueous solution, warmed with platinum black, evolves oxygen and yields brucine oxide, which can be reconverted into the peroxide by hydrogen peroxide. In 3% hydrogen peroxide the substance has $[\alpha]_D$ $-5·12°$, and yields with dilute sulphuric acid mainly the sulphate of brucine oxide. Sulphurous acid eliminates the active oxygen from the peroxide, leaving a mixture of brucine and *allo*-brucine.

Strychnine peroxide is obtained with some difficulty from strychnine and 14% hydrogen peroxide. The air-dried crystals contain $4H_2O$, two

of which are lost in a vacuum, the substance then having m. p. 178° (decomp.), and containing two atoms of active oxygen. The peroxide is almost completely dissociated in aqueous solution. In 95% alcohol it has $[\alpha]_D$ 9·7°. C. S.

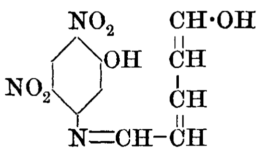
Action of Pyridine on 1:3-Dichloro-4:6-dinitrobenzene. THEODOR ZINCKE and G. WEISPFENNING (*J. pr. Chem.*, 1910, [ii], 82, 1—17).—By the action of hot pyridine on 1:3-dichloro-4:6-dinitrobenzene, Reitzenstein and Rothschild (Abstr., 1906, i, 454) obtained, together with dinitrophenyldipyridinium dichloride, a yellow condensation product, to which they assigned the constitution



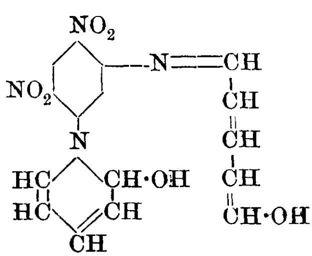
$$C_6H_2(NO_2)_2{<}{C_5NH_5\cdot O \atop C_5NH_5\cdot O}{>}C_6H_2(NO_2)_2.$$

This substance is now shown to be a betaine anhydride (annexed constitution), produced from the dinitrophenyldipyridinium dichloride by the action of the water present. It can also be prepared by the action of sodium nitrite on an aqueous solution of the dichloride, and by heating pyridine and 3-chloro-4:6-dinitrophenol at 100°. The addition of alcohol to solutions of the substance in moderately concentrated acids precipitates well characterised salts, of which the *chloride, chromate, platinichloride, nitrate*, and *sulphate* are described. It is converted into pyridine and dinitroresorcinol by 20% hydrochloric acid at 170°, and into pyridine and chlorodinitrophenol by hydrogen chloride in glacial acetic acid at 150°.

The action of excess of 2*N*-sodium hydroxide on an aqueous solution of the chloride of the condensation product yields a red substance, $C_{11}H_9O_6N_3$, which has not the constitution given to it by Reitzenstein and Rothschild, but that annexed, the substance being formed by rupture of the pyridine ring (compare Zincke, Abstr., 1904, i, 921). It is reconverted into the yellow betaine anhydride by hydrogen chloride in glacial acetic acid at 100°, and is decomposed by hot hydrochloric acid, yielding 4:6-dinitro-3-aminophenol, and by hot aniline, yielding the dinitroaminophenol and the dianilide, NPh:CH·CH:CH·CH:CH·NHPh, previously described.



Dinitrophenyldipyridinium dichloride forms colourless prisms containing $2H_2O$, which decompose by heating, pyridine, hydrogen chloride, and the yellow anhydride being produced. An aqueous solution, by treatment with sodium carbonate, or, better, with ammonium hydroxide, becomes violet, and finally deposits a blackish-green precipitate of a *substance*, $C_{16}H_{14}O_6N_4$, which forms red salts (the *chloride, platinichloride, bromide*, and *nitrate* are described), and receives the annexed constitution,



one pyridine ring being ruptured and the other converted into the ψ-form. The substance yields the yellow betaine anhydride by treatment with boiling glacial acetic acid and acetic anhydride, and is decomposed by boiling $2N$-hydrochloric acid, yielding 4 : 6-*dinitro*-3-*aminophenylpyridinium chloride*, $C_{11}H_9O_4N_4Cl$, m. p. 230—235° (decomp.). The blackish-green substance is also decomposed by aniline, yielding dinitrodiaminobenzene and the dianilide mentioned above. C. S.

Quinoline Sulphosalicylate. GEORGES PRUNIER (*J. Pharm. Chim.*, 1910, [vii], 1, 538—539).—*Quinoline sulphosalicylate*,

$$HSO_3{\cdot}C_6H_3(OH){\cdot}CO_2H,C_9H_7N,H_2O,$$

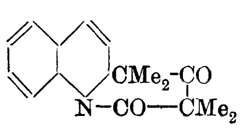
obtained by the action of the acid on the base in presence of water, melts partly at 110° and becomes anhydrous, and then melts at 220°. It crystallises in colourless, silky tufts, is sparingly soluble in cold water (1·547 parts per 100 at 17°), more so in warm water or alcohol, and is acid in reaction. It is poisonous in doses of 0·29 to 0·34 gram per kilogram of body-weight when applied subcutaneously or intravenously. Its antiseptic power is about the same as that of phenol, and its bactericidal action somewhat less. Its reactions with a number of common reagents are tabulated. T. A. H.

Ketens. II. Dimethylketen Bases. HERMANN STAUDINGER, HELMUT W. KLEVER, and P. KOBER (*Annalen*, 1910, **374**, 1—39. Compare Abstr., 1907, i, 424; 1908, i, 318).—An investigation of the keten bases formed by the combination of dimethylketen with tertiary bases.

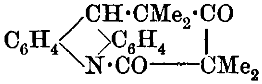
The dimethylketen bases, as a general rule, when treated with dilute mineral acids or alkalis, unite with a molecule of water, yielding acids having the composition 1 mol. base + 1 mol. keten + 1 mol. water or 1 mol. base + 1 mol. keten + 1 mol. *iso*butyric acid respectively. The corresponding esters and anilides of the acids may be obtained by acting on the keten base with an alcohol or aniline. The acids are converted by hot strong mineral acids into 2 mols. of *iso*butyric acid and 1 mol. of the tertiary base, and decompose when heated at a high temperature; for example, dimethylketenquinoline decomposes into quinoline and *iso*butyric anhydride.

The reactivities of the dimethyl-keten bases and of the acids derived from them varies with the nature of the tertiary base; thus, the pyridine compounds are very unstable, the derivatives of the quinoline series less reactive, whilst keten-acridine is so stable that it does not yield an acid, neither is it possible to decompose it with the formation of acridine and *iso*butyric acid.

Although the several reactions of dimethylketenquinoline may be satisfactorily accounted for by means of the constitutional formula advanced in a previous paper (compare Abstr., 1907, i, 424), nevertheless this formula is shown to be incorrect and must be replaced by the annexed formula, for it is found that Schiff's bases combine with 2 mols. of keten, the combination taking place through the C:N– linking. It is for this reason that only tertiary bases containing the C:N– group combine with dimethylketen; in the case of



acridine, it is probable that the formation of the keten base results through the fission of the para-linking, the base having the annexed formula.



Generally speaking, Schiff's bases combine with dimethylketen, yielding β-lactams, which undergo further change into β-amino-acids; benzylidenebenzylamine, however, in addition to the normal β-lactam, yields two other substances having the composition 1 mol. of Schiff's base + 2 mols. of dimethylketen, of which one, the chief product of the reaction, possesses the same characteristics as the dimethylketen bases already discussed. It is shown that this substance is 2 : 4-diketo-6-phenyl-1-benzyl-3 : 3 : 5 : 5-tetramethylpiperidine, since the acid formed by the action of a dilute solution of sodium carbonate on the keten base is identical with the substance obtained by treating the corresponding ester of β-benzylamino-β-phenyl-$\alpha\alpha$-dimethylpropionic acid with *iso*-butyric anhydride.

Benzylidenemethylamine, in analogy to benzylidenebenzylamine, reacts with dimethylketen, yielding as chief product a keten base.

Dimethylketenquinoline (compare Abstr., 1907, i, 424), when heated with dilute hydrochloric acid on a water-bath, yields an *acid*,

$$CH{<}\begin{matrix}CH—CH\cdot CMe_2\cdot CO_2H\\ C_6H_4\cdot N\cdot CO\cdot CHMe_2\end{matrix},$$

which forms colourless, compact crystals, m. p. 152—153°; many derivatives of the acid have been described previously (*loc. cit.*).

Dimethylketen-β-naphthaquinoline, $C_{21}H_{21}O_2N$, forms white crystals, m. p. 163°; the *acid* derived from it, $C_{21}H_{23}O_3N$, crystallises in white needles, m. p. 171°.

*Dimethylketen*iso*quinoline*, $C_{17}H_{19}O_2N$, crystallises in leaflets and needles, m. p. 105°; it gives rise to an *acid*, $C_{17}H_{21}O_3N$, which forms white crystals, m. p. 138°. The *acid*, $C_{13}H_{19}O_3N$, derived from dimethylketenpyridine, crystallises in large, colourless, prisms, m. p. 94—95°.

2 : 4-*Diketo*-6-*phenyl*-1-*benzyl*-3 : 3 : 5 : 5-*tetramethylpiperidine*,

$$CO{<}\begin{matrix}CMe_2\cdot CHPh\\ CMe_2——CO\end{matrix}{>}N\cdot CH_2Ph,$$

prepared from dimethylketen and benzylidenebenzylamine, could not be isolated in a pure state; it is converted by a hot aqueous solution of sodium carbonate chiefly into β-iso*butyrylbenzylamino-β-phenyl-$\alpha\alpha$-dimethylpropionic acid*, $CHMe_2\cdot CO\cdot N(CH_2Ph)\cdot CHPh\cdot CMe_2\cdot CO_2H$, which forms colourless crystals, m. p. 169·5° (decomp.); the *silver* salt is a crystalline, white powder. The acid is decomposed by boiling concentrated hydrochloric acid, yielding benzylamine, β-benzylamino-β-phenyl-$\alpha\alpha$-dimethylpropionic acid, *iso*butyric acid, benzaldehyde, dimethylstyrene, and *benzylbutyramide*, $C_{11}H_{15}ON$, white leaflets, m. p. 92°. Oxidation of the acid by potassium permanganate leads to the formation of *iso*butyric acid, benzoic acid, and a *substance*, $C_{22}H_{25}O_3N$, obtained as a white, crystalline powder, m. p. 195°. The following derivatives of the acid were prepared either from the acid or from the keten base by the usual methods: *methyl* ester, $C_{23}H_{29}O_3N$, large, colourless prisms, m. p. 109°; *ethyl* ester, $C_{24}H_{31}O_3N$, m. p. 111—112°; *bromide*, an amorphous powder which could not be

purified; *anilide*, $C_{28}H_{32}O_2N_2$, a white, crystalline powder, m. p. 138°; *phenylhydrazide*, $C_{28}H_{33}O_2N_3$, colourless, felted needles, m. p. 155°.

The *lactam* of *β-benzylamino-β-phenyl-αα-dimethylpropionic acid*, $CMe_2<\begin{matrix}CHPh\\CO\end{matrix}>N\cdot CH_2Ph$, is formed, together with *iso*butyric acid, by heating the acid just described at 180°; it forms large, white prisms, m. p. 36°, and is not altered by a hot alcoholic solution of phenylhydrazine or hydroxylamine, but is converted by an alcoholic solution of potassium hydroxide into the salt of the corresponding acid; the solution of the potassium salt thus obtained, when acidified with acids, yields the corresponding salts; the *acetate*, $C_{18}H_{21}O_2N,Me\cdot CO_2H$, is a white, crystalline powder, m. p. 190—191° (decomp.); the *hydrochloride*, $C_{18}H_{21}O_2N,HCl$, forms crystalline nodules, m. p. 142°. The *amino-acid* is obtained by dissolving the acetate in a known excess of aqueous sodium hydroxide, and adding the requisite quantity of hydrochloric acid; it crystallises with $1H_2O$ in small, white needles, m. p. 138—142°; the anhydrous substance has m. p. 145—148°; the *ethyl* ester, $C_{20}H_{25}O_2N$, prepared from the silver salt and ethyl iodide, has m. p. 63—64°. Attempts to replace the hydrogen of the NH-group by the *iso*butyryl group by heating the acid with *iso*butyryl chloride led to the formation of the β-lactam. The *iso*butyryl group can be introduced, however, by heating the ethyl ester with *iso*butyric anhydride.

The formation of 2 : 4-diketo-6-phenyl-1-benzyl-3 : 3 : 5 : 5-tetramethylpiperidine from dimethylketen and benzylidenebenzylamine is accompanied by the formation of the β-lactam just described, together with a *substance*, $C_{22}H_{25}O_2N$, m. p. 117°, which is extremely stable towards acids and alkalis.

Dimethylketen-benzylidenemethylamine, 2:4-*diketo*-6-*phenyl*-1:3:3:5:5-*pentamethylpiperidine*, prepared from dimethylketen and benzylidenemethylamine, could not be obtained pure; when heated with an aqueous solution of sodium carbonate, it yields the corresponding *acid*, $C_{16}H_{23}O_3N$, a white, crystalline powder, m. p. 142° with evolution of *iso*butyric acid; the *methyl* ester, $C_{17}H_{25}O_3N$, crystallises in white needles, m. p. 78°. The acid, when heated at 150°, yields the *lactam* of *β-methylamino-β-phenyl-αα-dimethylpropionic acid*, $C_{12}H_{15}ON$, an oil, b. p. 139·5°/13 mm.; the corresponding *acid*, $C_{12}H_{17}O_2N$, is obtained as a crystalline powder, m. p. 260°, which is possibly an internal ammonium salt. A *substance*, $C_{16}H_{21}O_2N$, is formed as a by-product in the interaction of dimethylketen and benzylidenemethylamine; it forms crystals, m. p. 115°. W. H. G.

Researches on Benzidine Formation. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 527—538).—A résumé of results already published, in part, in Abstr., 1905, i, 651; 1906, i, 314; 1909, i, 747. The following new compounds are described: 2 : 2'-*Dinitro*-4 : 4'-*diacetylaminodiphenylmethane*, $CH_2[C_6H_3(NO_2)\cdot NH_2]_2$, m. p. 229°, forms yellow crystals, and on reduction with stannous chloride yields the corresponding 2 : 2'-*diamino*-compound, m. p. 244°, which crystallises in colourless needles from dilute alcohol.

4 : 4'-Tetramethyldiamino-2 : 2'-azodiphenylmethane, on reduction

with stannous chloride in hydrochloric acid, furnishes 4 : 4′-tetramethyldiamino-2 : 2′-diaminodiphenylmethane (Pinnow, Abstr., 1895, i, 98), and this on further reduction with zinc dust and sodium hydroxide gives 4 : 4′-tetramethyldiaminoacridine (Biehringer, Abstr., 1897, i, 73).

T. A. H.

Action of Hypochlorous Acid and of Sodium Hypochlorite on Hydantoin and Acetylenediureine. HEINRICH BILTZ and OTTO BEHRENS (*Ber.*, 1910, **43**, 1984—1996. Compare Abstr., 1909, i, 848).—Sodium hypochlorite reacts with hydantoins and acetylenediureines, so that the H of one NH-group becomes replaced by Cl, and that of the second NH-group by Na; thus diphenylhydantoin yields $\begin{matrix}CPh_2\cdot NCl \\ | \\ CO-NNa\end{matrix}\!\!>\!CO$. If, however, an excess of free hypochlorous acid is used, both hydrogens are replaced by chlorine, and a compound of the type $\begin{matrix}CPh_2\cdot NCl \\ | \\ CO-NCl\end{matrix}\!\!>\!CO$ is formed. The chlorides can be crystallised from chloroform, but react readily with hydroxyl compounds, for example, with ethyl alcohol the original hydantoin is formed, together with acetaldehyde and chlorine. They also react readily with an aqueous solution of potassium iodide liberating iodine; the reaction proceeds in the two stages: (1) $>NCl + H_2O \rightleftarrows >NH + HOCl$; (2) $HOCl + 2HI = HCl + H_2O + I_2$. All the chlorides obtained are colourless and odourless, like most *N*-halide derivatives of acylamines, whereas *N*-halogenated alkylamines have pungent odours.

1 : 3-*Dichloro*-5 : 5-*diphenylhydantoin*, $\begin{matrix}CPh_2\cdot NCl \\ | \\ CO-NCl\end{matrix}\!\!>\!CO$, crystallises in well-developed, six-sided prisms, m. p. 164° (decomp.). It crystallises from benzene with $\frac{1}{2}C_6H_6$, which it loses at 108°. When methylated by means of methyl sulphate and dilute alkali, it yields 5 : 5-diphenyl-1 : 3-dimethylhydantoin (Biltz and Rimpel, Abstr., 1908, i, 462). 1-*Chloro*-5 : 5-*diphenyl*-3-*methylhydantoin*, $\begin{matrix}CPh_2\cdot NCl \\ | \\ CO-NMe\end{matrix}\!\!>\!CO$, prepared by the action of sodium hypochlorite on 5 : 5-diphenyl-3-methylhydantoin, crystallises in prisms, m. p. 186° (decomp.). 1 : 3-*Dichloro*-5 : 5-*dibromophenylhydantoin*, $\begin{matrix}(C_6H_4Br)_2C-NCl \\ | \\ CO\cdot NCl\end{matrix}\!\!>\!CO$, crystallises in rhombic plates, m. p. 241° (decomp.), and can be readily methylated, and yields the same 5 : 5-*dibromophenyl*-1 : 3-*dimethylhydantoin*, $C_{17}H_{14}O_2N_2Br_2$, m. p. 199°, as is obtained by methylating di-5-bromophenylhydantoin itself, or by condensing dibromobenzil with dimethylcarbamide at 210°.

4 : 5-*Dibromophenyl*-1 : 3-*dimethylglyoxalone*-4 : 5-*glycol*,

$$\begin{matrix}C_6H_4Br\cdot C(OH)\cdot NMe \\ | \\ C_6H_4Br\cdot C(OH)\cdot NMe\end{matrix}\!\!>\!CO,$$

obtained by boiling a mixture of dibromobenzil and *s*-dimethylcarbamide with sodium ethoxide solution for two hours, crystallises in rhombic plates, m. p. 212°. When heated at its m. p., it loses water and yields 5 : 5-dibromophenyl-1 : 3-dimethylhydantoin.

5 : 5-*Dibromophenyl-3-methylglyoxalone*, $(C_6H_4Br)_2C<\begin{matrix}NH\\CO\cdot NMe\end{matrix}>CO$ (with the C and CO joined), is obtained by boiling dibromobenzil and methylcarbamide with an alcoholic solution of sodium ethoxide for three hours, and crystallises in rhombic plates or prisms, m. p. 267°.

1-*Chloro*-5 : 5-*dibromophenylhydantoin*, $(C_6H_4Br)_2C\begin{matrix}-NCl\\|\\CO\cdot NH\end{matrix}>CO$, obtained by the action of carbon dioxide on its sodium derivative, crystallises in compact rhombohedra, m. p. 203° (decomp.). When diphenylthiohydantoin is treated with sodium hypochlorite and then with carbon dioxide, diphenyldichlorohydantoin is obtained.

1 : 3 : 7 : 9-*Tetrachloro*-4 : 5-*diphenylacetylenediureine*,

$$CO<\begin{matrix}NCl\cdot CPh\cdot NCl\\|\\NCl\cdot CPh\cdot NCl\end{matrix}>CO,$$

crystallises in six-edged prisms, m. p. 249° (decomp.).

1-*Chloro-3-sodium*-4 : 5-*diphenylacetylenediureine*,

$$CO<\begin{matrix}NCl-CPh\cdot NH\\|\\NNa\cdot CPh\cdot NH\end{matrix}>CO,$$

crystallises in long, glistening prisms, and, when carbon dioxide is passed into its aqueous solution, yields 1-*chloro*-4 : 5-*diphenylacetylenediureine*, $C_{16}H_{13}O_2N_4Cl$, which crystallises from acetone in six-sided prisms, m. p. 218° (decomp.).

Acetylenediureine is not so stable towards sodium hypochlorite, and at 95° yields 30% of free nitrogen. 4 : 5-Dimethylacetylenediureine behaves in a similar manner. J. J. S.

Catalytic Racemisation of Optically Active Hydantoin Derivatives and of Related Substances as the Result of Tautomeric Change. HENRY D. DAKIN (*Amer. Chem. J.*, 1910, **44**, 48—60).—In *N*-sodium hydroxide the rotation of the active hydantoins,

$$CHR<\begin{matrix}NH\cdot CO\\|\\CO-NH\end{matrix}$$

(where R is $\cdot CH_2Pr^{\beta}$, p-$OH\cdot C_6H_4\cdot CH_2$, $\cdot CH_2\cdot CO_2H$, or $\cdot CH_2\cdot CH_2\cdot CO_2H$),

diminishes to zero in the course of many hours, the solutions then yielding the *i*-hydantoins by acidification. The rotation of the corresponding carbamido-acids remains constant in *N*-sodium hydroxide. The loss of activity of the hydantoins is most obviously explicable by enol-keto-desmotropy, $CH\cdot CO \rightleftarrows C:C\cdot OH$ (compare Wren, Trans., 1909, **95**, 1593), the correctness of the explanation being supported by the case of the hydantoin, $CMeEt<\begin{matrix}NH\cdot CO\\|\\CO-NH\end{matrix}$, obtained from *iso*valine, the rotation of which remains constant in *N*-sodium hydroxide.

The following new compounds have been obtained by evaporating active α-amino-acids with aqueous potassium cyanate, and boiling the resulting active hydantoic acids with 10% hydrochloric acid: d-iso-*Butylhydantoic acid*, m. p. 205—206° (decomp.), $[\alpha]_D^{20}$ 1·9° in *N*-sodium hydroxide ($c=3·15$), from *l*-leucine; l iso*butylhydantoin*, m. p. 212°,

$[\alpha]_D^{20}$ $-68\cdot2°$ in *N*-sodium hydroxide ($c = 1\cdot925$), becoming 0 after thirty hours; d-*methylethylhydantoin*, m. p. 172—173°, $[\alpha]_D^{20}$ 32° ($c = 1\cdot247$), from *l-iso*valine. C. S.

Two Isomeric Benzylglyoxalidones. HERMANN FINGER and W. ZEH (*J. pr. Chem.*, 1910, [ii], **82**, 50—60).—Two isomeric benzylglyoxalidones are obtained when benzyliminoethyl ether is employed in the reaction described previously (Abstr., 1906, i, 901; 1907, i, 876). 4-*Keto*-2-*benzyl*-4 : 5-*dihydroglyoxaline*,

$$CH_2Ph\cdot C\Big\langle{N{-}{-}CO \atop NH\cdot CH_2},$$

m. p. 143°, obtained by keeping the imino-ether and ethyl glycine at 20° for two hours, is a weak monoacidic base. It is decomposed by hydrochloric acid, D 1·12, at 130° into phenylacetic acid, glycine, and ammonia, reacts with boiling water to form a *substance*,

$$C_{10}H_{12}O_2N_2,$$

m. p. 176—177°, which is probably phenylacetylglycinamide, forms with *p*-nitrodiazobenzene chloride in the presence of sodium acetate 5-p-*nitrobenzeneazo*-2-*benzylglyoxalidone*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot CH\Big\langle{CO{-}{-}N \atop NH\cdot C\cdot CH_2Ph},$$

yellow needles, darkening at 235°, combines with phenylcarbimide to form a *phenylcarbamide*, $C_{17}H_{15}O_2N_3$, with phenylthiocarbimide to form a *phenylthiocarbamide*, $C_{17}H_{15}ON_3S$, yields a *dibenzoyl* derivative,

$$CH_2Ph\cdot C\Big\langle{N{-}{-}COBz \atop NBz\cdot CH},$$

m. p. 138°, with benzoyl chloride in pyridine, *benziminylbenzylglyoxalidone*, $NH{:}CPh\cdot N\Big\langle{CH_2{-}{-}{-}CO \atop C(CH_2Ph){:}N}$, sulphur-yellow leaflets, m. p. 237°, with benziminoethyl ether, 5-*benzyl*-2-*benzylideneglyoxalidone*, m. p. 177·5°, with benzaldehyde in faintly alkaline solution, condenses with diacetyl to form a reddish-orange *substance*, $C_{14}H_{14}O_2N_2$, decomposing at 196°, and reacts with isatin in hot glacial acetic acid to form a scarlet indigoid *dye*,

$$NH\Big\langle{CO \atop C_6H_4}\Big\rangle C{:}C\Big\langle{CO{-}{-}N \atop NH\cdot C\cdot CH_2Ph},$$

which is reduced by alkaline hyposulphite to a yellowish vat-dye, oxidising rapidly in air.

The isomeric substance, iso*benzylglyoxalidone*, $C_{10}H_{10}O_2N_2$, m. p. 222° (decomp.), which is the chief product of the reaction when benzyliminoethyl ether and ethyl glycine are heated together, is probably the cyclic amidine, $CH_2Ph\cdot C\Big\langle{N{-}{-}CH_2 \atop NH\cdot CO}$. It is not attacked by boiling water, yields phenylacetic acid, glycine, and ammonia when decomposed by hydrochloric acid at 140°, forms an *acetyl* derivative, m. p. 189° (not sharp), with acetic anhydride, gives successively yellow, greenish-blue, reddish-violet, and red colorations when heated with glacial acetic acid, and yields a *substance*, $C_{18}H_{16}O_2N_2$, by heating with sodium hydroxide and subsequent acidification. C. S.

Decomposition of Indigotin and of Indirubin by Alkalis. PAUL FRIEDLÄNDER and ERW. SCHWENK (*Ber.*, 1910, **43**, 1971—1975. Compare Fritzsche, *Annalen*, 1841, **39**, 79; Heumann and Bachofen, Abstr., 1893, i, 270; Hentschel, *ibid.*, 1900, i, 231).—The decomposition of indigotin by alkalis cannot take place according to the equation given by Henschel, as the amount of indoxyl is very small, and varies with the temperature and the length of time of heating. The indoxyl is a secondary decomposition product. Fritzsche's chrysanilic acid is not a primary decomposition product; it is formed by the condensing action of the added acid on anthranilic acid and indoxyl-2-aldehyde, both of which are present as potassium salts after the fusion. The two are separated by taking the dilute solution of the fused mass, freeing it from indoxyl, and pouring into cold dilute hydrochloric acid, which is continually stirred, and also covered with a layer of ether. The anthranilic acid is then present in the aqueous, and the aldehyde in the ethereal, solution.

Indoxyl-2-aldehyde, $C_6H_4<\substack{C(OH)\\NH}>C\cdot CHO$, crystallises from warm water or from a mixture of chloroform and light petroleum in glistening needles, which decompose at about 160°. It condenses with anthranilic acid in the presence of acids, yielding chrysanilic acid,

$$CO_2H\cdot C_6H_4\cdot N\colon CH\cdot C<\substack{C(OH)\\NH}>C_6H_4.$$

The decomposition of indigotin may be represented by the scheme:

$$C_6H_4<\substack{CO\\NH}>C\colon C<\substack{CO\\NH}>C_6H_4 \longrightarrow$$
$$C_6H_4<\substack{CO\\NH}>C(OH)\cdot C<\substack{C(ONa)\\NH}>C_6H_4 \longrightarrow$$
$$NH_2\cdot C_6H_4\cdot CO_2H + C_6H_4<\substack{C(OH)\\NH}>C\cdot CHO.$$

When indirubin is heated with concentrated sodium hydroxide at 150°, it is transformed into a sparingly soluble *sodium* salt,

$$C_{16}H_{11}O_3N_2Na,$$

from which acids liberate the *acid*, $C_{16}H_{12}O_3N_2$. This crystallises from nitrobenzene in long, glistening, yellow needles, m. p. above 295°. When heated at 150°, it yields carbon dioxide, aniline, and oxindole, and as it can be synthesised from anthranilic acid and oxindole-3-aldehyde, is represented as

$$CO_2H\cdot C_6H_4\cdot N\colon CH\cdot C<\substack{C(OH)\\C_6H_4}>NH.$$

The action of alkali on indirubin is thus analogous to its action on indigotin:

$$C_6H_4<\substack{CO\\NH}>C\colon C<\substack{CO\\C_6H_4}>NH \longrightarrow$$
$$C_6H_4<\substack{CO\\NH}>C(OH)\cdot C<\substack{C(ONa)\\C_6H_4}>NH \longrightarrow$$
$$CO_2H\cdot C_6H_4\cdot N\colon CH\cdot C<\substack{C(OH)\\C_6H_4}>NH.$$

Oxindole-3-aldehyde, $C_6H_4<\substack{C(CHO)\\NH}>C\cdot OH$, is prepared readily by the action of alkalis on thioindigo-scarlet (3′-indoxyl-2-thionaphthen-

3-one: Bezdzik and Friedländer, Abstr., 1908, i, 673), the other product being *o*-thiolbenzoic acid. The aldehyde crystallises from dilute alcohol in pale yellow needles, m. p. 213°, and is more stable than indoxyl-2-aldehyde. J. J. S.

Condition of Indigo-White in Aqueous Solutions. EDMUND KNECHT and J. P. BATEY (*J. Soc. Dyers*, 1910, **28**, 171—173).—Calcium indigo-white has been shown by the boiling-point method to be crystalloid in solution. A solution of purified monosodium indigo-white is found to be an electrolyte. The material was prepared by mixing alcoholic sodium hydroxide with an excess of alcoholic indigo-white in an atmosphere of hydrogen, evaporating to dryness, and treating the residue with air-free water for two and a-half hours. The indigo-white in the solution, determined by oxidation and direct weighing, was very slightly in excess of the proportion required for pure monosodium salt.

The molecular conductivity of monosodium indigo-white is 62·6 at 19·35 litres and 67·7 at 37·85 litres dilution, that is, about 2/3 the conductivity of sodium chloride.

Cotton adsorbs indigo-white and sodium hydroxide in approximately equivalent proportions from a solution of monosodium salt, but more indigo and more alkali are adsorbed in presence of excess of sodium hydroxide. No definite relation between the amounts of indigo and alkali taken up in these cases could be found, but as nearly all the indigo can be washed out with air-free water, the action is doubtless an adsorption by the cotton. R. J. C.

Condensation of Phenyl*iso*oxazolone with Ethyl Mesoxalate. ANDRÉ MEYER (*Compt. rend.*, 1910, **150**, 1765—1767. Compare Abstr., 1908, i, 368).—When an alcoholic solution of ethyl mesoxalate (1·1 mol.) is boiled for thirty minutes with phenyl*iso*-oxazolone, a good yield of *ethyl bisphenyl*iso*oxazolonemesoxalate*,

$$C(CO_2Et)_2\left(CH{<}\begin{matrix}CO-O\\ CPh{:}N\end{matrix}\right)_2,$$

is obtained. This compound crystallises in large octahedra, m. p. 187° (decomp.), and forms solutions in aqueous alkali hydroxides or carbonates, from which it is precipitated by the addition of mineral acids. The *sodium* salt, $C_{25}H_{20}O_8N_2Na_2$, occurs in hexagonal crystals; its aqueous solution gives a violet precipitate with ferric chloride; the *silver, lead, mercuric,* and *zinc* salts are insoluble. The *diethyl* derivative, $C_{29}H_{30}O_8N_2$, obtained by the action of ethyl iodide on the sodium salt, crystallises in slender needles, m. p. 200—201°. The *diacetyl* derivative forms prisms, m. p. 166°; the *dibenzoyl* derivative has m. p. 194°.

The addition of benzenediazonium chloride to a solution of the compound in alkali results in the formation of Claisen's benzeneazophenyl-*iso*oxazolone (Abstr., 1891, 468). W. O. W.

Action of Hydrazoic Acid on Some Acids of the Acetylene Series. Synthesis of Derivatives of 1 : 2 : 3-Triazole. E. OLIVERI-MANDALÀ and A. COPPOLA (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 563—569. Compare Oliveri, *ibid.*, 1905, [v], **14**, i, 228).—When an

ethereal solution of acetylenedicarboxylic acid (Perkin, Trans., 1907, 91, 834) is warmed for a short time with an ethereal solution of hydrazoic acid, 1 : 2 : 3-triazoledicarboxylic acid, identical with that of Bladin and of Zincke (Abstr., 1896, i, 550), is obtained. This substance yields with 3 molecules of diazomethane a *trimethyl* derivative, m. p. 55—60°, in which one of the methyl groups is attached to nitrogen, since it yields methylamine when boiled with concentrated alkali. Phenylpropiolic acid and hydrazoic acid react but slowly, only 7/10 of the substances having condensed after six days at 45—50°. The behaviour of this acid with hydrochloric acid is similar (Michael and Pendleton, Abstr., 1889, 1063). The product, 4-*phenyl*-1 : 2 : 3-*triazole*-5-*carboxylic acid*, has m. p. 205—206°, decomposing into carbon dioxide and phenyltriazole. Analysis indicated the presence of $\frac{1}{2}H_2O$, but it was not possible to eliminate this from the substance. The *barium* salt crystallises with $2H_2O$. 4-*Phenyl*-1 : 2 : 3-*triazole*, obtained by heating the above acid at 210—215°, has m. p. 143—145°, and displays both basic and acid properties; it yields a *silver* salt, dissolves in dilute alkalis, and is precipitated again by acids; it forms a *hydrochloride*, m. p. about 140°, and a *platinichloride*. 1 : 2 : 3-Triazolecarboxylic acid (Dimroth, Abstr., 1902, i, 403) can be prepared similarly. R. V. S.

Decomposition of Certain Cyclic Imines by means of Sodium Hypochlorite HEINRICH BILTZ and OTTO BEHRENS (*Ber.*, 1910, **43**, 1996—1999).—Allantoin, 3-methylallantoin, 5-hydroxy-1 : 3-dimethylhydantoylcarbamide (Biltz, this vol., i, 521), 7 : 9-dimethyluric acid glycol, and parabanic acid give almost theoretical amounts of nitrogen at the ordinary temperature in the presence of sodium hypochlorite solution and excess of potassium hydroxide. Uric acid and its methyl derivatives under similar conditions evolve nitrogen slowly, and in most cases the amount of nitrogen corresponds with the non-methylated imino-groups present. An exception is 7-methyluric acid.

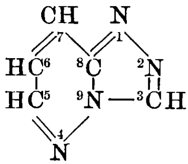
Alloxan also reacts but slowly with hypochlorite. Methyl- and dimethyl-carbamides react only slowly with hypochlorite. J. J. S.

Methylation and Constitution of Allantoin. HEINRICH BILTZ (*Ber.*, 1910, **43**, 1999—2003. Compare Siemonsen, Abstr., 1904, i, 951).—3-Methylallantoin can be prepared by the action of methyl iodide on the silver salt of allantoin. Although the yield is only 33% of the theoretical, this is probably the most convenient method for the preparation for the 3-methyl derivative. 3-Methylallantoin is not reduced so readily as allantoin, and after treatment with 1% sodium amalgam in slightly acid solution, yields carbamide, 3-methylhydantoin, and unaltered substance.

The behaviour of allantoin towards sodium hypochlorite, namely, the elimination of two of the four atoms of nitrogen, is in harmony with Grimaux's formula, $NH_2\cdot CO\cdot NH\cdot CH<\begin{matrix}NH\cdot CO\\ CO-NH\end{matrix}$. The alternative formula, hydroxyacetylenediureine, $CO<\begin{matrix}NH\cdot CH——NH\\ NH\cdot C(OH)\cdot NH\end{matrix}>CO$, cannot

be correct, as such a compound should be stable towards hypochlorite; further, allantoin gives none of the reactions characteristic of hydroxy-compounds. J. J. S.

Heterohydroxylic Acids. CARL BÜLOW and CARL HAAS (*Ber.*, 1910, i, 43, 1975—1984. Compare Abstr., 1909, i, 613—616; this vol., i, 80—81).—As heterohydroxylic acids are denoted the compounds formed by the condensation of 1-amino-1 : 3 : 4-triazole with the esters of γ-carboxylic acids. The hydroxylic group in position 7 (annexed formula of 1 : 2 : 4 : 9-benztetrazole) imparts pronounced acid properties to the compounds, so that they can be titrated readily with standard sodium hydroxide. A comparison of these hydroxylic acid compounds with ordinary carboxylic acid has been made. Their esters cannot be prepared by the ordinary catalytic method of esterification, by the action of alcohol on the corresponding chloride, or by the action of methyl sulphate on the alkali salts, but are formed when the silver salts are treated with alkyl iodides. They can be benzoylated by the Schotten-Baumann process, but the resulting benzoates are hydrolysed readily by dilute alkalis. A mixture of phosphorus pentachloride and oxychloride transforms the hydroxy-compounds into the corresponding chlorides, which are much more stable than ordinary acyl chlorides; they can be crystallised from alcohol or water, but react readily with potassium hydrogen sulphide, yielding thiols, which are readily oxidisable compounds with pronounced acidic properties. The chlorides form salts with strong acids, but these are fairly readily hydrolysed. The hetero-condensed, heterocyclic system is stable towards concentrated hydrochloric acid, and the acids may be heated with the hydrochloric acid at 140° without appreciable decomposition; but they are readily decomposed when fused with potash at 280°, one of the products being hydrogen cyanide.



7-Hydroxy-5-methyl-1 : 2 : 4 : 9-benztetrazole (compare Abstr., 1909, i, 615) is best prepared by heating 1-amino-1 : 3 : 4-triazole (11 grams) with ethyl acetoacetate (19 grams), first at 130°, then for one hour at 150°, and finally at 160—170° for a quarter to half an hour. The *sodium* salt, $C_6H_5ON_4Na$, crystallises from alcohol in colourless needles; the *ethyl* ester, $C_8H_{10}ON_4$, crystallises from a mixture of benzene and light petroleum, and has m. p. 170—171°; the *benzoate*, $C_{13}H_{10}O_2N_4$, crystallises from methyl alcohol in long prisms containing methyl alcohol, or from ethyl acetate in cubes, m. p. 157—158°. *7-Chloro-5-methyl-1 : 2 : 4 : 9-benztetrazole*, $C_6H_5N_4Cl$, crystallises in long, yellow, glistening needles, m. p. 185°; the corresponding *iodide*, $C_6H_5N_4I$, crystallises in large, colourless needles, m. p. 211—212°, and forms a *hydriodide*, m. p. 196—197°, which is obtained when the hydroxy-compound is boiled for six hours with concentrated hydriodic acid and red phosphorus.

5-Methyl-1 : 2 : 4 : 9-benztetrazole-7-thiol,

$$\begin{matrix} CMe{:}N——N{\cdot}CH \\ | \qquad\quad | \\ CH{:}C(SH){\cdot}C{=}N \end{matrix} \!\!>\! N,3H_2O,$$

crystallises in long, yellow needles, sinters at 150°, but is not com-

pletely molten at 280°; its aqueous solution when boiled in contact with the air yields a brown, amorphous, flocculent mass.

When the chloride is reduced with zinc dust and water, 5-*methyl-1:2:4:9-benztetrazole*, $\begin{array}{l}\mathrm{CMe{:}N\cdot N\cdot CH} \\ | \quad\quad\quad\; | \\ \mathrm{CH{:}CH\cdot C{=}N}\end{array}\!\!>\!\mathrm{N}$, is formed, and can be isolated as the *picrate*, $C_6H_6N_4,C_6H_3O_7N_3$, which crystallises in yellow cubes, m. p. 162—163°. The base crystallises in colourless needles, m. p. 158—159°.

When the hydroxy-compound is heated with five times its weight of phenylhydrazine, it yields 4-anilinoazo-1-phenyl-3-methyl-5-pyrazolone (this vol., i, 233) together with other products. The hydroxy-compound reacts with hydrazine, yielding a *salt*, $C_6H_6ON_4,N_2H_4$, which crystallises from alcohol in large, glistening plates. J. J. S.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. III. GUSTAV HELLER (*Ber.*, 1910, 43, 1907—1922. Compare Abstr., 1908, i, 867, 913).—[With EDMUND WEIDNER]—The reduction of *o*-nitrobenzamide by zinc dust and 50% acetic acid leads to the formation of small quantities of o-*azoxybenzamide*, m. p. 242° (decomp.), and o-*azobenzamide*, m. p. 284—294° (decomp.), the chief product, however, being benz*iso*oxazolone, which from this method of formation might have the constitution

$$\text{I. } C_6H_4{<}\begin{array}{l}\mathrm{N(OH)} \\ \;| \\ \mathrm{CO}\end{array} \quad \text{or} \quad \text{II. } C_6H_4{<}\begin{array}{c}\mathrm{NH} \\ \mathrm{CO}\end{array}{>}O.$$

The first formula harmonises with the amphoteric character of the substance and with the formation of acetyl, benzoyl, and methyl derivatives, but since Reissert's 1-acetoxyoxindole (Abstr., 1909, i, 51), an undoubted *N*-hydroxy-derivative, is reduced to oxindole by zinc dust and 50% acetic acid, whilst 2-acetylbenz*iso*oxazolone is reduced to acetylanthranilic acid, there is no alternative but to accept formula II for benz*iso*oxazolone, a conclusion to which Bamberger and Pyman have arrived at on other grounds (Abstr., 1909, i, 573). *o*-Azobenzamide, when treated with cold concentrated sulphuric acid and sodium nitrite and subsequently heated, yields *benzamide*-o-*azobenzoic acid*,

$$NH_2\cdot CO\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CO_2H,$$

m. p. 215° (decomp.), and is reduced by glacial acetic acid and zinc dust to o-*hydrazobenzamide*, $N_2H_2(C_6H_4\cdot CO\cdot NH_2)_2$, m. p. 233°.

The reduction of ethyl *o*-nitrobenzoate by acetic acid and zinc dust yields only ethyl *o*-azoxybenzoate. The reduction of *o*-nitrobenzyl alcohol by zinc dust and 50% acetic acid at 0° and subsequently at 40° yields *o*-azoxybenzyl alcohol and *o*-azobenzyl alcohol.

[With WALTER TISCHNER].—*o*-Nitrophenyl-lactaldehyde is reduced to quinoline by zinc dust, glacial acetic acid, and its own weight of water. *o*-Nitrobenzaldehydediethylacetal is reduced to anthranil, and β-*o*-nitrophenyl-α-methyl-lactaldehyde, prepared from *o*-nitrobenzaldehyde and propaldehyde, is reduced in a similar manner to 2-methylquinoline, the *hydrochloride*, C_9NH_6Me,HCl, of which has m. p. 228—230°, and the *mercurichloride*, $3C_9NH_6Me,HCl,2HgCl_2$, m. p. 164—165°.

The reduction of *o*-nitrocinnamic acid by zinc dust and acetic acid in the presence of sodium acetate and water at 40—45° yields about 10%

of *o-azoxycinnamic acid*, m. p. 218° (decomp.), and 50% of *o*-aminocinnamic acid. An aqueous solution of the hydrochloride of the latter and acetic anhydride yields *o-acetylaminocinnamic acid*, m. p. 248—249° (decomp.), which forms carbostyril when heated, and by warming for one hour with acetic anhydride produces *bis-o : o-diacetylaminocinnamic anhydride*, $(NAc_2·C_6H_4·CH:CH·CO)_2O$, m. p. 156—157°. *o-Diacetylaminocinnamic acid*, obtained by heating the anhydride with aqueous sodium acetate and a little acetic acid, has m. p. 158°.

Dibromo-*o*-nitrophenylpropionic acid is readily reduced by zinc dust, glacial acetic acid, and its own weight of water at 0°, yielding *o*-aminocinnamic acid and a little *o*-azoxycinnamic acid. C. S.

Bisazo- and Trisazo-derivatives of Resorcinol. WILLIAM R. ORNDORFF and B. J. RAY (*Amer. Chem. J.*, 1910, **44**, 1—41).—2 : 4 : 6-*Trisbenzeneazoresorcinol*, m. p. 254°, obtained from diazotised aniline hydrochloride (3 mols.) and resorcinol in sodium hydroxide solution, and also from 4 : 6-bisbenzeneazoresorcinol or from 2 : 4-bisbenzeneazoresorcinol and benzenediazonium chloride (1 mol.) in sodium hydroxide solution, crystallises in yellowish-brown, pleochroic needles, and when boiled with acetic anhydride and sodium acetate forms a *diacetyl* derivative, which separates from its solutions in yellow needles, m. p. 201°, by rapid cooling, or in red, pyramidal crystals, m. p. 203°, by slow cooling, and is reconverted into trisbenzeneazoresorcinol by powdered potassium hydroxide suspended in ether.

Wallach and Fischer's β-bisbenzeneazoresorcinol is shown to be 2 : 4 : 6-trisbenzeneazoresorcinol contaminated with 4 : 6-bisbenzeneazoresorcinol, and, similarly, their β-bis-*p*-tolueneazoresorcinol to be a mixture of 2 : 4 : 6-tris-*p*-tolueneazoresorcinol (the diacetyl derivative crystallises in yellow needles, m. p. 218°, or in red crystals, mutually interconvertible) and 4 : 6-bis-*p*-tolueneazoresorcinol (*diacetyl* derivative, m. p. 198·5°). 2 : 4-*Bis-p-tolueneazoresorcinol*, m. p. 230·5°, prepared from diazo-*p*-toluene chloride (2 mols.) and resorcinol in sodium acetate solution, forms a *diacetyl* derivative, m. p. 150°.

2 : 4 : 6-*Tris-o-tolueneazoresorcinol*, m. p. 226°, forms a diacetyl derivative, m. p. 176°. 4 : 6-Bis-*o*-tolueneazoresorcinol has m. p. 197° (Wallach gives m. p. 194—195°), and forms a *diacetyl* derivative, m. p. 178°. 2 : 4-*Bis-o-tolueneazoresorcinol*, m. p. 212°, prepared like the para-isomeride, forms a *diacetyl* derivative, m. p. 130°.

2 : 4 : 6-*Tris-a-naphthaleneazoresorcinol*, m. p. 253° (*diacetyl* derivative, yellow prisms, m. p. 228°, or red, tabular crystals, mutually interconvertible), 2 : 4-*bis-a-naphthaleneazoresorcinol*, m. p. 242° (*diacetyl* derivative, m. p. 142°), and *bisbenzeneazo-p-diazoaminoazobenzene*, $N(N_2·C_6H_4·N_2Ph)_2·C_6H_4·N_2·Ph$, m. p. 184°, are also described; the last-mentioned substance is obtained by adding cold alcoholic aminoazobenzene (3 mols.) and acetic acid (9 mols.) to cold sodium nitrite (2 mols.). C. S.

Heat Coagulation of Proteins. HARRIETTE CHICK and CHARLES J. MARTIN (*J. Physiol.*, 1910, **40**, 404—430).—Crystallised egg-albumin and hæmoglobin were used in the experiments. They are not coagulated by dry heat up to 130°. Heat coagulation is therefore not purely a tem-

perature effect, but a reaction between water and protein. The rate of coagulation of hæmoglobin solutions is proportional to the concentration of the residual hæmoglobin, in the case of egg-albumin, the rate decreases more rapidly than can be accounted for in this way; the crystals are doubtless not homogeneous, and changing conditions are also introduced by the adsorption of acid by the coagulum. Egg-albumin crystals are, as Osborne stated, salts of protein with the acids used in their preparation. Details are given confirmatory of Halliburton's statements as to the effect of acid in hastening the rate of coagulation; it is very considerable. Coagulation of proteins is influenced by temperature in accordance with the law of Arrhenius, but the temperature-coefficient is very high, namely, 1·91 per degree for egg-albumin and 1·3 for hæmoglobin.

It is not correct to speak of proteins having any particular coagulation-temperature. Heat coagulation is a reaction between protein and water, and the effect of temperature is merely to accelerate it. Given constant conditions, however, the method may still be used to differentiate proteins, and even to separate them if two proteins are possessed of different reaction rates. The optimum temperature for enzyme actions is also interpreted in a simple way: two operations are at work, that produced by the enzyme, and the destruction of the enzyme by water. If the influence of the temperature on the latter process is greater than on the former, the effect of the enzyme action is counteracted as the temperature rises, and a point is finally reached when the rate of destruction is so great that the enzyme action is arrested. W. D. H.

Analysis of Proteins. ALEXANDRÉ ETARD and ANTONY VILA (*Compt. rend.*, 1910, **150**, 1709—1711. Compare Abstr., 1908, i, 584; 1909, i, 124).—After removing diamino-acids from the products of hydrolysis of proteins by the method already described, another group of amino-acids may be precipitated by means of ferrocyanic acid.
W. O. W.

Analysis of Edestin and Zein. THOMAS B. OSBORNE and L. M. LIDDLE. **Sources of Loss in Analysing the Products of Protein Hydrolysis.** THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1910, **26**, 295—304, 305—328).—A number of incomplete analyses of the two proteins mentioned are described in the first paper. The second paper, as its title indicates, should be studied in detail by those interested in protein analysis. The following table of cleavage products of zein is considered nearer the truth than any previously published.

Glycine	0 00	Tyrosine	3 55
Alanine	9 79	Arginine	1 55
Valine	1 88	Histidine	0 82
Leucine	19 55	Lysine	0 00
Proline	9 04	Tryptophan	0 00
Phenylalanine	6 55	Ammonia	3 64
Aspartic acid	1 71	Carbohydrate	0 00
Glutamic acid	26 17		
Serine	1 02	Total	85 27

W. D. H.

Fibrin-ferment. C. GESSARD (*Compt. rend.*, 1910, **150**, 1617—1618. Compare Abstr., 1909, ii, 682).—Whilst hæmoglobin is freed from hæmase by a single crystallisation, the operation must be repeated several times to remove the fibrin-ferment. The latter is carried down by calcium phosphate when this is precipitated from a solution of fibrin (obtained by whipping) in physiological salt solution. After washing the calcium phosphate, the fibrin-ferment may be extracted by maceration with horse serum, previously heated for an hour at 60°.

W. O. W.

Behaviour of Hæmoglobin towards Hydrazine and the Question of the Capacity of the Colouring Matter of Blood for Combining with Gases. E. LETSCHE (*Zeitsch. physiol. Chem.*, 1910, **67**, 177—191).—The experiments of Hüfner have been repeated and extended (Abstr., 1889, 426; 1900, i, 267; *Arch. Anat. and Physiol.*, 1894, 156). The spectrophotometric method has been used, and the values of ϵ'/ϵ for hæmoglobin with and without the addition of hydrazine hydrate determined under different conditions. The results show that it is the hydrazine and not some impurity which reacts with the hæmoglobin. The effect of the addition of hydrazine hydrate can also be detected by the naked eye. Methæmoglobin is also affected by hydrazine. Both changes consist partially of reductions, but other reactions take place at the same time.

Hæmoglobin and hæmin solutions behave quite differently towards hydrazine, and the reactions are being subjected to further examination.

The effect of the presence of hydrazine on the solubility of carbonic oxide in hæmoglobin has been studied. Also, the effects of concentration of the hæmoglobin solution and of pressure have been examined (compare Manchot, this vol., ii, 137). Some of the differences found can be explained on the view that the solution of the gas is partly physical, and thus the solubility falls under Henry's Law, but chemical combination also occurs.

J. J. S.

Colouring Matter of Blood. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1910, **67**, 195—196).—Polemical in reply to Küster (this vol., i, 529).

J. J. S.

Oxidation of Pure Oxyhæmoglobin by Hydrogen Peroxide. I. SZRETER (*Compt. rend.*, 1910, **151**, 97—99. Compare Abstr., 1909, i, 620).—Hydrogen peroxide acts on oxyhæmoglobin at 37°, bringing about simple addition of oxygen, and converting it into a substance which, after purification by dialysis, was obtained in colourless, brilliant spangles containing 0·98% of iron in organic combination. Before dialysis, the substance was hygroscopic and much less stable.

W. O. W.

Behaviour of *d*-Leucyl-*l*-tryptophan towards Autolytic Ferments. HANS FISCHER (*Ber.*, 1910, **43**, 1963—1964).—The author confirms his previous statement that *d*-leucyl-*l*-tryptophan is attacked by autolytic ferments, including yeast extract.

Abderhalden and Schuler's seemingly negative results (this vol.,

i, 304) are attributable to the fact that the products of hydrolysis have much the same rotation as the original peptide. J. J. S.

Chondroitinsulphuric Acid. KURA KONDO (*Biochem. Zeitsch*, 1910, **26**, 116—130).—The acid was prepared from the cartilage of the nasal septum of pigs, which was treated first with 2% potassium hydroxide for two days. The alkaline liquid, after filtration, was just acidified with acetic acid, and boiled with barium carbonate; this treatment was continued until the whole of the protein was coagulated, and the liquid, after filtration and concentration, was thrown into three times the volume of glacial acetic acid; after solution of the precipitate thus formed in water and reprecipitation with glacial acetic acid, the free acid thus obtained was neutralised with sodium or potassium hydroxide, the solution concentrated, and the sodium or potassium salt precipitated by the addition of alcohol. The composition of the acid prepared thus corresponded approximately with the formula $C_{15}H_{27}O_{16}NS$. It gave strongly the orcin and phloroglucinol reactions, and yielded furfuraldehyde after treatment with acids. It gave also, but in very small yield, an osazone-like substance, melting at 143°. The salts are lævorotatory. The benzoyl derivatives of the scission products obtained by treatment of the chondroitinsulphuric acid with 2—3% hydrochloric acid were also investigated. The product obtained did not contain more than five benzoyl groups. S. B. S.

Lipoids. X. The Detection of Galactose in Lipoids. SIGMUND FRÄNKEL and KURT LINNERT (*Biochem. Zeitsch.*, 1910, **26**, 41—43).—The authors isolated the galactose obtained by the hydrolysis of brain lipoids in the form of the α-phenylmethylhydrazone, which melted at 189°. They also isolated the sugar by hydrolysing with sulphuric acid, separating the acid after hydrolysis by barium hydroxide and carbonate, evaporating the filtrate, dissolving the residue from evaporation in methyl alcohol, and then adding ether. After several days, the sugar could be separated in crystalline form. S. B. S.

Lipoids. XII. The Phosphatides of Horse Pancreas. SIGMUND FRÄNKEL and THEODOR R. OFFER (*Biochem. Zeitsch.*, 1910, **26**, 53—54).—From hot acetone extract of horse pancreas a crystalline substance separates on cooling, which, after filtering from liquid fats, washing with 90% alcohol, and recrystallising from hot absolute alcohol, melts at 120°. Two grams were obtained from 4½ kilos. of the fresh organ. The analyses corresponded with the formula $C_{72}H_{147}O_{11}N_2P$; the substance is a saturated diaminomonophosphatide. S. B. S.

The Protective Action of Proteins on Enzymes. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, **26**, 9—13).—The addition of proteins (egg-white) protects enzymes from the deleterious action of acids and bases. This protective action could be demonstrated in the cases of δ-emulsin, diastase and invertin. S. B. S.

The Inactivation of Ferments, and the Formation of Anti-ferments in Presence of Collodium and Other Membranes. ALBERT E. PORTER (*Biochem. Zeitsch.*, 1910, **25**, 301—304).—The

investigations included the study of pepsin, trypsin, rennet, steapsin, ptyalin, emulsin, and taka-diastase. All these ferments, with the exception of taka-diastase, lose their activity in presence of collodion membranes, and acquire, with the exception of ptyalin, an antifermentative action. Colloids other than collodion, such as egg-white membranes and gelatin, exert a similar action. S. B. S.

Inversion of Sucrose by Invertase. IV. Influence of Acids and Alkalis on the Activity of Invertase. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1910, **32**, 774—779; *Zeitsch. Ver. deut. Zuckerind.*, 1910, 634—641. Compare Abstr., 1908, i, 605, 856; 1909, i, 554).—The work described in this paper was undertaken with the object of determining the conditions of acidity and alkalinity which render invertase inactive, and also those which cause its total destruction.

It has been found that acids and alkalis in small concentrations influence the activity of invertase, whilst in large concentrations they cause its destruction. The destruction by acid at 30° proceeds at a scarcely appreciable rate at a concentration of $0{\cdot}01N$, and increases rapidly with the acidity until it becomes almost instantaneous at $0{\cdot}05N$. The rate of destruction follows the formula for unimolecular reactions. The destruction by alkali at 30° commences at a point a little below $0{\cdot}01N$, and is almost instantaneous at $0{\cdot}045N$. The rates of destruction are plotted as curves.

The activity of invertase in acid solutions which are not strong enough to destroy the enzyme have been determined for hydrochloric, hydrobromic, nitric, phosphoric, sulphuric, boric, oxalic, tartaric, citric, and acetic acids. The activity has been found to depend almost entirely on the concentration of hydrogen ions in the solution. The activity of invertase is zero in alkaline solutions, rises to a maximum in very weakly acid solutions, and decreases with increasing acidity. E. G.

Invertase. Niro Masuda (*Zeitsch. physiol. Chem.*, 1910, **66**, 145—151. Compare Salkowski, Abstr., 1909, i, 752).—The addition of yeast gum to an invertase solution which is free, or nearly free, from gum increases the activity of the enzyme to a slight, although perceptible, extent. Invertase solutions (that is, filtered yeast extract) lose almost 70% of their activity on keeping for twenty-four hours, but the activity then diminishes only very slowly. Old preparations full of moulds and bacteria retain their inverting power. Invertase produces slightly more invert sugar in 10% than in 5% sucrose solution. Increase of the amount of ferment does not produce a proportional increase in the amount of invert sugar formed. E. F. A.

Destruction of Invertase by Acids and Alkalis. H. S. Paine (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, **7**, xli—xlii).—Invertase was placed at 30° in various concentrations of hydrochloric acid and sodium hydroxide for different times. All samples were then brought to the optimum acidity in sucrose solutions of the same strength and volume. Action was allowed to take place

for an hour, and the velocity-coefficient calculated from the formula for unimolecular reactions; from this the coefficient of the rate of destruction was derived.

Destruction commenced at about 0·015*N*-acid and 0·01*N*-alkali solution, requiring five to six hours for completion. In 0·05*N*-acid and 0·04*N*-alkali destruction occurred in five minutes. W. D. H.

Studies on Enzyme Action. XIII. Enzymes of the Emulsin Type. HENRY E. ARMSTRONG and EDWARD HORTON (*Proc. Roy. Soc.*, 1910, *B*, **82**, 349—367. Compare Abstr., 1908, i, 745).—Contrary to the statement of Dunstan, Henry, and Auld (Abstr., 1907, ii, 572), it is shown that phaseolunatin, the glucoside present in *Phaseolus lunatus* seeds, in flax seed, and in cassava is invariably hydrolysed by almond-emulsin, although only to a very small extent. Moreover, amygdalin is found to be as little attacked by the *Phaseolus* enzyme (phaseolunatase) as is phaseolunatin by emulsin, when the comparison is made under molecularly similar conditions.

The observation made by Dunstan, Henry, and Auld (*loc. cit.*), that methyl-α-glucoside is hydrolysed by phaseolunatase, is not confirmed. Similarly, the enzyme was found to be inactive towards maltose. Methyl-β-glucoside, however, is attacked by phaseolunatase, although much less readily than by emulsin, an observation which has not hitherto been recorded.

The authors confirm the statement of Dunstan and his co-workers, that phaseolunatin is hydrolysed by an extract of dried yeast, but attribute this to the action, not of maltase, but of the "emulsin" discovered in yeast by Henry and Auld (Abstr., 1906, ii, 114).

The conclusion arrived at by Dunstan, Henry, and Auld, that phaseolunatin is an α-glucoside, is controverted by the authors. Experiments are described which tend to indicate that the glucose is liberated from phaseolunatin in the β-form, but the question is complicated by the fact that the enzyme itself suffers a change in optical rotatory power when treated with the small quantity of alkali necessary to effect the mutarotation of the liberated glucose. Since all efforts to discover in *Phaseolus* seeds an enzyme capable of effecting the hydrolysis of α-glucosides failed, the conclusion is drawn that phaseolunatin is a β-glucoside, and that the correlated enzyme phaseolunatase is of the β-type.

Although only very slightly active towards amygdalin, phaseolunatase is almost as active as almond-emulsin towards *l*-mandelonitrileglucoside. This may be partly accounted for by the absence from phaseolunatase of amygdalase, but no explanation is offered of the fact that, whilst phaseolunatase attacks both phaseolunatin and *l*-mandelonitrileglucoside equally, almond-emulsin acts only very slightly on the former glucoside.

Pressed yeast juice and the enzyme extracted from *Anthyllis vulneraria* seed are similarly more active towards *l*-mandelonitrile glucoside than towards amygdalin, and only act very slightly on phaseolunatin. The differences in the activity of vegetable cytase towards the three cyanophoric glucosides are less marked, although in the same direction.

It is pointed out that the experiments assumed by Auld (Trans., 1908, **93**, 1277) to prove that the glucose liberated from amygdalin by yeast extract is in the α-form, whilst that set free when *l*-mandelonitrile glucoside is hydrolysed is in the β-form, are invalidated by the fact that both glucosides are racemised fairly rapidly by alkali, with consequent change in their optical rotatory powers.

A comparison is given of the results obtained when estimating hydrogen cyanide by the method devised by the authors, and by the modification of Fordos and Gelis' method employed by Dunstan and his colleagues. From this it seems that the latter method is only to be preferred in the estimation of quite minute amounts of hydrogen cyanide.

The authors advocate the employment, in experiments with hydrolytic enzymes, of solutions (of the various hydrolytes) of the same molecular concentration, in order that the concordance between the results obtained by different workers (when this exists) may be rendered apparent. E. H.

The Separation of the Racemic Cyanohydrins by Emulsin. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, **26**, 7—8. Compare Abstr., 1909, i, 74).—*l*-Benzaldehydecyanohydrin can be obtained from the racemic variety by the action of δ-emulsin when air is led through the mixture. This has the effect of removing one of the products of hydrolysis, namely, the hydrogen cyanide. S. B. S.

Asymmetric Syntheses by means of Enzymes. III. Leopold Rosenthaler (*Biochem. Zeitsch.*, 1910, **26**, 1—6).—In addition to the method already described, namely, by heating for a long time at 40—50°, for separating the δ- (hydrolysing) emulsin from the σ- (synthesising) enzyme, the author finds that a separation can also be accomplished by treating the mixtures of enzymes for a short time with acids and then neutralising with alkali. The quantity of acid and time of action must be determined for every sample of emulsin investigated, and great variations are found in the different preparations. The author also describes various other methods attempted for separating the enzymes, which did not lead to the desired effect. S. B. S.

Biology of Enzymes. Action of Heat on the Lipases and Amylases of Pancreatic Juice. Sabato Visco (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 597—603).—The lipolytic power of pancreatic juice was determined by adding to it sweet almond oil and titrating with alcoholic sodium hydroxide the oleic acid formed after the mixture had been a certain time in a thermostat. The amylolytic power was measured by estimating the sugar formed from starch in similar circumstances. It was found that the lipase slowly changes at the ordinary temperature, and loses its activity completely in a few hours at 39—41°. The ferment is not affected by the higher temperature, however, if it has already commenced to act on the oil. The amalyse, when kept at 39—41°, at first shows slightly increased activity, but the latter diminishes, although slowly, on prolonged exposure to that temperature. R. V. S.

Plant Peroxydases. I. New Method of Preparing Peroxydases. A. W. van der Haar (*Ber.*, 1910, **43**, 1321—1327).—Bach (Abstr., 1908, i, 746; this vol., i, 291) has claimed that both peroxydases and oxydases can be obtained absolutely free from manganese and iron. Peroxydase has now been purified by the author a stage further than by Bach, until all coagulable protein had been removed, but it has not been possible to remove absolutely all manganese. After precipitation of impurities by basic lead acetate, the proteins can be coagulated by heating the solution to 90° without destroying the peroxydase. Throughout the process of purification the oxidising power was contrasted with the amount of manganese present, but no relation between these two factors was evident. E. F. A.

Plant Peroxydases. II. Hedera-Peroxydase, a Glucoprotein. A. W. van der Haar (*Ber.*, 1910, **43**, 1327—1329).—A carefully purified peroxydase preparation from the leaves of *Hedera helix* contained 2% of ash, and the solution, which lacked other known enzymes, showed the biuret, xanthoprotein, and Millon's reactions; it contained organically combined nitrogen and sulphur, but was free from phosphorus. When boiled with 3% hydrochloric acid, it acquired the power of reducing Fehling's solution, and formed a phenylosazone, m. p. 165°. In addition, the peroxydase was non-coagulable, and could not be salted out. It is regarded in consequence as a glucoprotein. It contained 0·0007% of manganese, equivalent to 0·03% of the ash. The peroxydase from potatoes also yielded a carbohydrate on treatment with acids. E. F. A.

Action of Haloid Derivatives of Sulphur on Organo-magnesium Compounds. Enos Ferrario [and, in part, H. Vinay] (*Bull. Soc. chim.*, 1910, [iv], **7**, 518—527).—The investigation of the action of sulphur chloride, dichloride, and tetrachloride on aromatic and aliphatic magnesium haloid compounds showed that sulphurisation, chlorination, and condensation proceeded simultaneously; thus with sulphur dichloride the following reactions probably occurred: $2PhMgBr + SCl_2 = SPh_2 + 2MgBrCl$; $2PhMgBr + 2SCl_2 = 2PhCl + 2MgBrCl + S_2$; $4PhMgBr + 2SCl_2 = 2Ph-Ph + 4MgBrCl + S_2$; $2PhS{\cdot}MgBr + SCl_2 = S_3Ph_2 + 2MgBrCl$. The products of the reaction were separated by fractional distillation under diminished pressure.

The mixture, obtained by the action of sulphur chloride on magnesium phenyl bromide and the addition of water, contained chlorobenzene, bromobenzene, phenyl sulphide, diphenyl and phenyl disulphide, trisulphide, and tetrasulphide. Sulphur dichloride with the same compound furnished the same products as did also sulphur tetrachloride, except that in the latter case more chlorobenzene was formed. In this reaction the tetrachloride behaved as a mixture of sulphur dichloride and chlorine.

Sulphur chloride reacted with magnesium methyl iodide to give methyl chloride and methyl sulphide, disulphide, and trisulphide. The action with magnesium ethyl bromide was analogous, ethyl chloride, sulphide, and disulphide being formed. T. A. H.

Organic Chemistry.

Critical Constants of Acetylene and Cyanogen. ETTORE CARDOSO and GEORGES BAUME (*Compt. rend.*, 1910, **151**, 141—143).—The following values have been obtained for the critical constants of pure acetylene and cyanogen. Acetylene has a critical temperature 35·5°, and critical pressure 61·5 atmospheres (compare Mathias, Abstr., 1909, ii, 552). Cyanogen has a critical temperature 128·3°; pressure, 59·6 atmospheres. The author considers that the cyanogen employed in Dewar's determinations was not free from air, and that consequently the results obtained were too low (Abstr., 1885, 331).

W. O. W.

The Decomposition of Certain Salts of Silver. ANGELO ANGELI and L. ALESSANDRI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 784—793. Compare Abstr., 1909, i, 739).—The dinitro-derivatives of stilbene have been stated to be converted into resins by the action of alkali, whilst the compounds obtained by the authors from the silver salt of ω-*iso*nitrotoluene yield definite compounds. It is now shown that the action of sodium ethoxide on α-dinitrostilbene yields the compound $OEt\cdot CHPh\cdot CHPh\cdot NO_2$, identical with that obtained by the authors, and yielding the compound $CHPh:CPh\cdot NO_2$ when acted on with piperidine.

Other nitro-derivatives react in a similar manner. The silver salt of nitroethane decomposes, yielding a *dinitrobutane*,

$$NO_2\cdot CHMe\cdot CHMe\cdot NO_2,$$

which melts at 41° and decomposes at 150°, but may be distilled under reduced pressure. At the same time a small quantity of the compound $CHMe:CMe\cdot NO_2$ appears to be formed.

The pure dinitro-compound is decomposed by potassium methoxide, but the original oil yields large, bright yellow crystals of a salt, $C_8H_8O_5N_4K_2$, apparently a condensation product.

It was not found possible to reduce the dinitrobutane directly to diacetyldioxime, a hydroxylamine derivative being formed, which is not readily oxidised to the dioxime. The reduction may, however, be effected by means of zinc dust and acetic acid in alcohol, concentrating the filtrate, and adding hydrochloric acid, followed by the addition of an excess of ammonium chloride, ammonia, and nickel sulphate, afterwards passing a current of air. A heavy, pink precipitate of the nickel compound of diacetyldioxime is obtained (Tschugaeff, Abstr., 1905, ii, 613), and yields the dioxime when decomposed with acid.

The silver salt of nitropentane yields colourless prisms of *dinitrodecane*, $C_{10}H_{20}O_4N_2$, m. p. 109—110°.

Piperonaldoxime, nitrocinnamene, and phenyldiazonitroethane also yield unstable salts, but definite compounds have not been isolated from their products of decomposition. C. H. D.

Action of Metallic Oxides on the Primary Alcohols. PAUL SABATIER and ALPHONSE MAILHE (*Ann. Chim. Phys.*, 1910, [viii], **20**, 289—352).—Mainly a résumé of work published by the present authors and others (compare Jahn, Abstr., 1880, 794; Grigorieff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 173; *Bull. Soc. chim.*, 1902, [iii], **26**, 612; Ipatieff, Abstr., 1901, i, 248; 1902, i, 335; 1903, i, 593; Sabatier and Mailhe, Abstr., 1908, i, 594, 713; 1909, i, 546; this vol., i, 294; Senderens, Abstr., 1908, ii, 166; 1909, i, 127, 286; Sabatier and Senderens, 1905, i, 333, 401). Contrary to the statement made previously (Abstr., 1909, i, 546), methyl alcohol when decomposed by titanium oxide gives formaldehyde.

A table is given showing the composition of the gas evolved, and its rate of evolution, when a fixed quantity of ethyl alcohol is decomposed by the various oxides examined.

An explanation similar to that proposed for the decompositions effected by finely divided metals is suggested for the catalyses produced by the oxides. E. H.

Preparation of Pyruvic Acid. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, **43**, 2188—2189).—A 60% yield of pure pyruvic acid, b. p. 59—60°/12 mm., can be obtained by distilling a mixture of 500 grams of tartaric acid and 780 grams of commercial potassium hydrogen sulphate from a copper retort of about 2 litres capacity. The process requires about thirty minutes, and no frothing occurs. As the metal is corroded by the sulphate, it is advisable to cover the interior of the retort with asbestos paper and water glass. The receiver is well cooled, and is provided with an upright condenser, the upper end of which is closed with a plug of cotton wool. The crude distillate is purified by fractional distillation under reduced pressure. J. J. S.

Degradation of Cholic Acid. II. The Distillation Products of Cholic and Bilianic Acids. OTTO VON FÜRTH and EMIL LENK (*Biochem. Zeitsch.*, 1910, **26**, 406—434).—Two main products were obtained by the distillation both of cholic and bilianic acid, the one of oily and the other of wax-like nature. The oily product is a hydrocarbon with something between 12 and 17 carbon atoms (as it gave varying numbers for the molecular weight determined by the ebullioscopic method in various solvents). It readily resinifies. The wax-like substance contains oxygen. The authors give an account of the action of halogens of permanganate and of nitric acid on the oily substance. No products have yet been isolated in a pure state. S. B. S.

Preparation of Cystine. OTTO FOLIN (*J. Biol. Chem.*, 1910, **8**, 9—10).—Cystine is easily prepared from wool by the following method, which differs mainly from Möurer's in the use of strong acid; 200 c.c. of strong hydrochloric acid to each 100 grams of wool are boiled in a flask (with a condenser consisting of a tube 2 or 3 feet long) until the biuret test is negative, usually three to five hours. Solid sodium acetate is added until the Congo-red reaction for mineral acid

is negative; a dark heavy precipitate, which contains practically all the cystine is obtained; this is filtered and washed with cold water. The filtrate on keeping deposits a second precipitate, consisting mainly of tyrosine. The crude cystine is dissolved in 3 to 5% hydrochloric acid and decolorised with bone-black, which has been previously digested with dilute hydrochloric acid to remove the calcium phosphate. The filtrate is heated to boiling, and the cystine precipitated by the slow addition of hot concentrated sodium acetate solution. W. D. H.

Action of Ozone on Organic Compounds. II. CARL D. HARRIES (*Annalen*, 1910, **374**, 288—368. Compare Abstr., 1906, i, 225).—The paper contains a discussion of work published during the last five years on the mode of attack of ozone on various classes of organic compounds, the behaviour of ozone derivatives during fission by water or other reagents, the constitution of the ozonides, the special behaviour towards ozone of substances containing different kinds of double linkings, the behaviour of the solvent during ozonisation, a description of the ozonising apparatus, and the effect of varying concentrations of ozone.

The following new work is described. Ethyl alcohol has been ozonised in the hope of showing that the first step in the oxidation is the formation of Baeyer and Villiger's ethyl hydroperoxide, EtO·OH. The *substance* obtained, however, is not identical with, but must be nearly allied to, ethyl hydroperoxide; possibly it is the tautomeric peroxide, $\genfrac{}{}{0pt}{}{Et}{H}{>}O{:}O$. It has b. p. 55—56°/10 mm., $D_{21.5}^{21.5}$ 1·028, n_D 1·40924, explodes violently when heated, contains 11·3% of active oxygen, reduces Fehling's solution and ammoniacal silver nitrate, and yields hydrogen peroxide and acetaldehyde when decomposed by water. The oxidation of β-hydroxypropioacetal by ozone yields β-hydroxypropaldehyde, not the semi-acetal of malondialdehyde as previously stated (Harries, Abstr., 1904, i, 15).

[By RUDOLF KOETSCHAU.]—Langheld has shown that by direct ozonisation heptaldehyde yields a peroxide, $C_7H_{14}O_2$. When treated with 15% ozone in ethyl chloride, or with 7% ozone in methyl chloride, the aldehyde yields a *substance*, D_{17}^{17} 0·9504, n_D^{17} 1·42867, the composition of which approximates to the formula $C_7H_{14}O_3$. Similarly, octaldehyde, when ozonised in ethyl chloride by 15% ozone, yields a *peroxide*, $C_8H_{16}O_2$, D_{19}^{19} 0·9088, n_D^{19} 1·42767, or by more prolonged action a *substance*, D_{19}^{19} 0·9497, n_D^{19} 1·43267, approximating to the composition $C_8H_{16}O_3$. By direct ozonisation with 7% ozone at 0°, nonaldehyde yields a *peroxide*, $C_9H_{18}O_2$, m. p. 6°, which is not identical with the peroxide, m. p. 73°, obtained by the decomposition of oleic acid ozonide; in methyl chloride the aldehyde is converted by 7% ozone into a *substance*, D_{21}^{21} 0·9334, n_D^{21} 1·43167, the composition of which approximates to $C_9H_{18}O_3$. *iso*Valeraldehyde yields a *peroxide*, $C_5H_{10}O_2$, D_{23}^{23} 0·9462, n_D^{23} 1·40826, by direct treatment with 15% ozone in a freezing mixture, and a *substance*, $C_5H_{10}O_3$(?), n_D^{21} 1·40335, when ozonised in ethyl chloride. *iso*Butaldehyde and acetaldehyde behave in a similar manner. Formaldehyde in methyl chloride is quantitatively

converted into trioxymethylene by treatment with ozone. By treatment with sodium hydroxide, the preceding peroxides are converted into the sodium salts of the corresponding acids. The fatty acids do not yield per-acids by treatment with ozone, but are merely oxidised.

[With H. O. Türk.]—To the results obtained by Harries and Türk by the exhaustive ozonisation of mesityl oxide and phorone (Abstr., 1905, i, 413) the following are to be added. By treatment with 12—14% ozone in an atmosphere of dry carbon dioxide, mesityl oxide, cooled by a freezing mixture, yields a normal *ozonide*, $C_6H_{10}O_4$, $D_{18·5}^{18·5}$ 1·0754, $n_D^{18·5}$ 1·39409, which is decomposed by water, yielding acetone, methylglyoxal, and formic and acetic acids; when carefully heated at 105°, the ozonide yields carbon dioxide, acetone, acetone peroxide, formic and acetic acids, methylglyoxal, and mesityl oxide, which is identified in the form of its *p*-nitrophenylhydrazone.

By ozonisation in carbon tetrachloride, care being taken to avoid an excess of ozone, methylheptenone yields a normal *ozonide*, $C_8H_{14}O_4$, which resembles Langheld's perozonide in many respects. It is decomposed by water, yielding acetone peroxide, acetone, lævulic acid, lævulaldehyde (isolated as phenylmethyldihydropyridazine), and a small amount of a peroxide of the last.

Mesoxaldialdehyde, in the form of its *tris*-p-*nitrophenylhydrazone*, m. p. 297° (decomp.), has now been definitely detected amongst the products of decomposition of phorone diozonide by water (compare Harries and Türk, *loc. cit.*). When a chloroform solution of phorone is incompletely ozonised, a *monozonide* seems to be formed, since dimethylacrylic acid occurs amongst its products of decomposition by water. Mesoxaldialdehyde, together with benzaldehyde and benzoic acid, is formed by decomposing with water the viscous, yellow oil formed by ozonising a chloroform solution of dibenzylideneacetone until the greenish-yellow colour has disappeared.

[By Karl Kircher.]—It has been stated previously (Harries and Kircher, Abstr., 1907, i, 466) that the ozonide of β-benzylidenelævulic acid is decomposed by water, yielding benzaldehyde, benzoic acid, and diacetylcarboxylic acid, and also that diacetylcarboxylic acid is a comparatively stable compound. It is now found that malonic acid is also present amongst the products of decomposition of the ozonide, and also that diacetylcarboxylic acid is an unstable substance, being partially decomposed even by the evaporation of its aqueous solution in a vacuum. Since the products of its decomposition are malonic and acetic acids, it seems very probable that the decomposition of β-benzylidenelævulic acid ozonide involves the production of a peroxide, thus:

$$\begin{array}{l} CHPh\cdot CAc\cdot CH_2\cdot CO_2H \\ O—O—O \end{array} \longrightarrow PhCHO + \begin{array}{c} O \\ | \\ O \end{array}\!\!>C<\!\!\begin{array}{l} CO\cdot CH_3 \\ CH_2\cdot CO_2H \end{array} \xrightarrow{H_2O}$$

$$CH_3\cdot CO_2H + CH_2(CO_2H)_2.$$

Diacetylcarboxylic acid forms a *bis*-p-*nitrophenylhydrazone*, m. p. 295° (decomp.), crystallising in red prisms, and a *bis-semicarbazone*, m. p. 240° (decomp.).

[By Walter Franck.]—Further information is given respecting the ozonides of oleic acid (compare Harries and Franck, Abstr., 1909, i, 131). The normal ozonide is always produced, independent of the concentration of the ozone, when care is taken, by testing with bromine

in acetic acid, to avoid any excess of the amount of ozone theoretically required; directly this limit is exceeded, the perozonide is formed. The normal ozonide is decomposed by hot glacial acetic acid, yielding nonaldehyde and its peroxide, nonolic acid, azelaic acid, and its peroxide and semialdehyde. Decomposition by glacial acetic and formic acids prevents the formation of peroxides, but otherwise gives the same products. The decomposition of an ethereal solution of the ozonide by moist ethereal sulphur dioxide or by aluminium amalgam also yields the same products. The normal ozonide of oleic acid forms salts, of which the *ammonium*, *sodium*, and *copper* salts are described, when care is taken to exclude moisture and to prevent rise of temperature. Nonaldehyde peroxide, m. p. 72°, b. p. 80—90°/13 mm., is changed to sodium nonoate by sodium hydroxide, and liberates only about 50% of the theoretical quantity of iodine from acidified potassium iodide in consequence of the change of about one-half of the peroxide into the isomeric acid.

When oleic acid is submitted to prolonged treatment with 10% ozone, or when its solution in glacial acetic acid is treated with 16—18% ozone for four hours, a *super-perozonide*, $C_{18}H_{34}O_7$, is formed, which has D_{22}^{22} 1·079, n_D^{22} 1·46817, is not particularly explosive, and yields by decomposition with warm water the same products as the other ozonides of oleic acid.

The normal *ozonide*, $C_{18}H_{34}O_6$, D_{20}^{20} 1·027, n_D^{20} 1·46171, of elaidic acid is prepared in a similar manner to, and does not differ in any respect from, the normal ozonide of oleic acid; it has not yet been settled whether the two are identical. C. S.

The Scission of Sugars. Synthesis of Sugar from Formaldehyde. WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1910, **26**, 231—237. Compare this vol., i, 95).—Experiments were carried out to determine whether the equilibrium between formaldehyde and the aldehydes with more carbon atoms (hexoses and pentoses) was the same in the building-up process from aldehydes as in the degrading processes from sugars, when the same substances are present at the same time in a mixture. The question could not be definitely answered, owing to the secondary process affecting only the formaldehyde, by means of which it was converted into methyl alcohol and acraldehyde. On treatment of formaldehyde solutions with lead hydroxide, a pentose seemed to be formed, which could not be isolated in the form of a pure osazone. Saccharic acid could be identified. S. B. S.

Phosphoric Esters of Some Polyhydric Alcohols and Carbohydrates. ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 823—827. Compare this vol., i, 157).—It is shown that certain polyhydroxylic compounds combine with phosphoric acid without undergoing any change of structure, a fact of importance in studying naturally occurring compounds.

When 25 grams of mannitol are heated for ten hours with 120 grams of phosphoric acid, D 1·7, to 120—130°, the product being decolorised with animal charcoal and purified by means of the barium

salt, a syrupy liquid, having the composition $C_6H_{20}O_{24}P_6$, is obtained, and is thus *mannitol hexaphosphate*. Quercitol yields a *pentaphosphate*, $C_6H_{17}O_{20}P_5$, whilst dextrose forms a *heptaphosphate*, $C_6H_{20}O_{28}P_7$, the aldehyde group behaving as two hydroxyl groups. C. H. D.

Phosphoric Acid Esters of Carbohydrates. II. Sucrosesulphuric Acid and the Phosphoration of Protein. CARL NEUBERG and HUGO POLLAK (*Ber.*, 1910, **43**, 2060—2068; *Biochem. Zeitsch.*, 1910, **26**, 514—534. Compare this vol., i, 157).—Dextrose dissolved in water and mixed with finely-divided calcium carbonate is well cooled and continuously shaken from eight to ten hours with phosphoryl chloride dissolved in chloroform. The liquid is then concentrated in a vacuum, and the *calcium salt* of *dextrose phosphoric acid ester* precipitated by pouring into alcohol. It is a colourless, soluble powder, stable in the atmosphere, and reduces Fehling's solution. It only shows the reactions of phosphoric acid after hydrolysis with boiling mineral acids, and is not fermentable until hydrolysed.

To prepare sucrosesulphuric acid, potassium pyrosulphate is slowly added to a mixture of sucrose and potassium hydroxide at 60—70°. After twenty-four hours, inorganic sulphuric acid is removed with barium hydroxide and *barium sucrosesulphate*, obtained as a colourless powder which only reduces Fehling's solution after hydrolysis. It has $[\alpha]_D^{29}$ +26·09°. The sulphuric acid is very firmly bound in the molecule, but if the equivalent quantity of cold hydrochloric acid is added to the barium salt, the liquid obtained reduces Fehling's solution after a time. The *calcium* salt is similar; it is not fermentable.

The simple amino-acids react with phosphoryl chloride in presence of alkali to form organic phosphoric acid compounds, but these could not be isolated. The proteins behave similarly, but in this case the phosphorus compounds are precipitated by acetic acid. These phospho-proteins are similar to the natural products, and are digested by trypsin and pepsin. E. F. A.

Stachyose and Lupeose. ERNST SCHULZE (*Ber.*, 1910, **43**, 2230—2234).—Lupeose (β-galactan: Abstr., 1892, 1171) from *Lupinus luteus* and *L. angustifolius* has the same optical rotation and gives the same yield of mucic acid on oxidation as stachyose, whereby saccharic acid is also formed. It is a tetrasaccharide composed of residues of galactose (2), dextrose, and lævulose, but since it cannot be caused to crystallise in the same way as stachyose, the two are not yet regarded as identical. When purified by pouring the aqueous solution into methyl alcohol, and precipitating this solution with absolute ethyl alcohol, it has $[\alpha]_D$ +148°. E. F. A.

Oxidation and Hydrolysis of Glycogen Under the Action of Hydrogen Peroxide. Mme. Z. GATIN-GRUŽEWSKA (*Bull. Soc. chim.*, 1910, [iv], **7**, 744—747. Compare Würster, Abstr., 1887, 683; Asboth, Abstr., 1893, i, 384; Gatin-Gruževska, Abstr., 1909, i, 209).—If a 1% solution (100 c.c.) of glycogen is mixed with pure hydrogen peroxide (5 c.c.) and kept at 37°, the opalescent liquid

gradually becomes more and more limpid, and at the end of five days is quite transparent, when it is no longer coloured by iodine. Under the same conditions, solutions of amylopectin take a shorter, and of amylose a longer, time to become transparent. The transparent solution, when treated with ten volumes of alcohol, gives a precipitate having all the properties of an achroodextrin, the amount of which diminishes and has entirely disappeared at the end of the twelfth day. The same changes occur if the liquid is previously rendered slightly alkaline with sodium hydrogen carbonate. The course of the oxidation can be traced by withdrawing samples from the solution at intervals of twenty-four hours and estimating the acidity by titration with standard alkali, whilst the undecomposed hydrogen peroxide may be estimated with permanganate. To determine the reducing power towards Fehling's solution, the hydrogen peroxide is first decomposed by adding platinum black to the neutralised sample.

Examination of the curves tracing the rate of decomposition of the hydrogen peroxide shows that 5 c.c. of hydrogen peroxide decompose most rapidly in 100 c.c. of water, only traces remaining after ten days, less rapidly in a 1% glycogen solution, about 16% being left at the end of twenty-three days, and still less rapidly in a starch solution, 50% being still undecomposed after twenty-three days. In more concentrated solutions the decomposition is more rapid, probably owing to the greater acidity and different character of the colloid. The change in the reducing power of glycogen is slower, and in acidity is faster, than the corresponding changes for starch. Whilst the action of hydrogen peroxide on glycogen is more energetic than that on starch, the converse is true of the action of the amylase from the pancreatic juice of the dog on these two substances. E. H.

New Method of Preparation of Primary and Secondary Amines from Ketones. KARL LÖFFLER (*Ber.*, 1910, **43**, 2031—2035).—By the action of ammonia or methylamine on ketones and subsequent reduction with sodium ethoxide, primary and secondary amines are readily obtained in good yields. It is assumed that the imine, $X_1X_2C{:}NR$, is the intermediate product of the change being formed by elimination of water between ketone and ammonia, or from a ketoammonia compound. Thus from acetone and ammonia a mixture of *iso*propylamine and di*iso*propylamine is formed; the formation of the latter is explained as due to the *iso*propylamine formed reacting with unchanged acetone in the same manner. *iso*Propylamine aurichloride (H_2O) forms matted plates, m. p. 72—73° [Fenner and Tafel (Abstr., 1900, i, 111) give m. p. 131—135°, which probably refers to the nearly dry salt]. The *aurichloride* of di-*iso*propylamine separates in masses of intergrown needles, m. p. 169—170°.

sec.-Amylamine is obtained in the same way from methyl propyl ketone and ammonia; the platinichloride forms glistening plates, decomp. 215°; the normal oxalate has m. p. 226°; the sulphate crystallises in colourless plates. E. F. A.

Synthetic Homocholine. FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, **67**, 296).—In reference to the work of Malengreau and

Lebailly on this subject (this vol., i, 545), it is pointed out that synthetic homocholine was prepared by Berlin in the author's laboratory, but his results are not yet published. W. D. H.

Additions to the Papers on ε-Amino-α-guanidinohexoic Acid and New Syntheses of Aminohydroxy-acids and of Piperidone Derivatives. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber*, 1910, 43, 2189—2192. Compare this vol., i, 100, 305).—The dihydrochloride of an anhydride of ε amino-α-guanidinohexoic acid was obtained by the decomposition of ε-benzoylamino-α-guanidinohexoic acid with hydrochloric acid. The free base, *ε-amino-α-guanidinohexoic anhydride*, $C_7H_{14}ON_4$, is a colourless, crystalline powder, which turns bright red at 175—185°, and decomposes at 190° to a brownish-yellow liquid. The *platinichloride* is a yellow, crystalline powder, which becomes grey at 220—230°, and decomposes at 230—240°.

The amorphous compound obtained by the hydrolysis of gelatin, previously described as possessing some points of resemblance to the synthetic β-hydroxy-α-piperidone, is now found to be a mixture of anhydrides of α-amino-acids. E. F. A.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XIV. Phosphorescence of Organic Sulphur Compounds by Spontaneous Oxidation. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1910, [iv], 7, 722—724).—In addition to the compounds containing the group $S\colon\dot{C}O\cdot$ already described (this vol., i, 295), which are phosphorescent by spontaneous combustion, *methyl sulphocarbonic chloride*, Cl·CS·OMe, b. p. 107—108°, and ethyl sulphocarbonic chloride, Cl·CS·OEt, are observed to fume in the air and phosphoresce strongly with an ozone-like odour. When the methyl ester is treated with magnesium methyl iodide, it gives the *compound*, Me·CS·OMe, b. p. 87—89°, which also fumes and phosphoresces strongly. The only compound, not containing the above group, which oxidises with brilliant phosphorescence is carbon chlorosulphide, $SCCl_2$. Methyl and ethyl methyl thiocarbonate, SMe·CO·OR, methyl ethyl thiocarbonate,

SEt·CO·OMe,

methyl dithiocarbonate, $CO(SMe)_2$, and methyl dimethothiocarbamate, $SMe\cdot CO\cdot NMe_2$, which contain the grouping $O\colon\dot{C}S\cdot$, and the iminothiocarbonic esters, NMe:C(SMe)·OMe, NMe:C(SEt)·OMe, and NEt:C(SMe)·OMe, which contain the grouping $\colon C{<}^{O\cdot}_{S\cdot}$ (see following abstract), do not phosphoresce. Tetramethyl-, tetraethyl-, and tetrapropyl-*iso*thiocarbimides, $NR\colon C(SR)\cdot NR_2$, and the isomeric tetra-alkylthiocarbamides, $CS[NR_2]_2$, which are formed by replacing the ·OR-group of the phosphorescent sulphocarbamic esters, NRR′·CS·OR, with the group ·NRR′, as well as the thiosulphocarbamic esters,

NRR′·CS·SR″,

are similarly inactive. The sulphocarbamic esters, $NH_2\cdot CS\cdot OR$ or NHR′·CS·OR, which contain a hydrogen atom combined with the nitrogen, do not, unlike their alkyl derivatives, phosphoresce by spontaneous oxidation.

It is suggested that the readiness with which the compounds con-

taining the group $S\dot{:}\dot{C}O\cdot$ are oxidised is due to the residual affinity of the sulphur and carbon atoms. E. H.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XV. Iminothiocarbonic Esters of the Aliphatic Series: $RN\dot{:}C(OR)(SR_1)$. Marcel Delépine (*Bull. Soc. chim.*, 1910, [iv], 7, 724—727).—Some of the iminothiocarbonic esters, which contain the grouping $\dot{:}C{<}^{S\cdot}_{O\cdot}$, have been prepared for comparison with the compounds (preceding abstract) containing the grouping $S\dot{:}\dot{C}\cdot O\cdot$, which are phosphorescent by spontaneous oxidation. Hitherto only the aromatic derivatives of this series have been prepared (compare Liebermann, Abstr., 1882, 296; Wheeler and Dustin, Abstr., 1901, i, 24).

When the sodium salts of the thiocarbamic esters prepared according to Roschdestvensky's method (this vol., i, 107) are treated with alkyl iodides they probably react in the tautomeric form, thus:

$$NR\dot{:}C(OR)\cdot SNa + IR' = NR\dot{:}C(OR)\cdot SR' + NaI,$$

giving the aliphatic iminothiocarbonic esters. The latter are colourless, mobile liquids, boiling almost 50° lower than, and appreciably less dense than, the corresponding iminodithiocarbonic esters, which they resemble in odour. The iminothiocarbonic esters are weak bases, soluble in dilute acids, but readily displaced by alkalis or ammonia, neutral to litmus and phenolphthalein, but exactly mono-acid towards helianthin. They are hydrolysed by boiling dilute acids into the amine and thiocarbonic ester. The iminothiocarbonic esters, like the dithio-compounds, lose the $\cdot SR'$ group when treated with silver nitrate or mercuric chloride.

Neither the iminothiocarbonic esters nor the sulphourethanes, $NHR\cdot CS\cdot OR'$, obtained intermediately, nor the thiocarbonic esters, $CO(OR)(SR')$, formed on hydrolysis, fume or phosphoresce when brought into contact with the air. The picrates of the first-named compounds form well-defined, yellow crystals.

Dimethyl methyliminothiolcarbonate, $NMe\dot{:}C(SMe)\cdot OMe$, a liquid, b. p. 142—144°, D_4^0 1·0654, D_4^{19} 1·0457, n_D^{20} 1·48458, when hydrolysed gives the hitherto unknown *methyl methyl thiolcarbonate*, $CO(SMe)\cdot OMe$, which is a colourless liquid having an ethereal odour, b. p. 120—121°, D_4^0 1·1452, $D_4^{21\cdot5}$ 1·1203, n_D^{23} 1·45242; the *picrate* of the former has m. p. 110°.

Methyl ethyl methyliminothiolcarbonate, $NMe\dot{:}C(SEt)\cdot OMe$, has b. p. 158—160°, D_4^0 1·0320, D_4^{19} 1·0125, $n_D^{20\cdot5}$ 1·48189; the *picrate* has m. p. 100°. *Dimethyl ethyliminothiolcarbonate*, $NEt\dot{:}C(SMe)\cdot OMe$, has b. p. 154—155°, D_4^0 1·02545, D_4^{19} 1·0056, $n_D^{20\cdot5}$ 1·47838; the *picrate* has m. p. 94°. Instead of the values previously given, the author finds for dimethyl thioncarbonate, $CS(OMe)_2$, D_4^0 1·13065, D_4^{24} 1·1028, n_D^{24} 1·45962. The latter compound is distinguished from the isomeride, $SMe\cdot CO\cdot OMe$, by reacting immediately with silver nitrate, silver sulphide being precipitated. E. H.

A Simple Method of Preparation of Pure Cyanamide. Fritz Baum (*Biochem. Zeitsch.*, 1910, 26, 325—332).—Seventy-five grams of

calcium nitride are stirred for half an hour with 400 c.c. of water. The process is repeated with a second quantity of water, which is finally used for treatment of a second batch of nitride. A third extract with water of the first batch is used for a second treatment of the second batch, and then for a first treatment of a third batch of nitride, etc. Finally, an extract is obtained which has been employed for treatment of four lots of nitride, and which is a strong solution of cyanamide. This is neutralised with sulphuric acid, separated from the precipitated calcium sulphate, and the liquid is then concentrated in a vacuum. On cooling, the residue crystallises, and the cyanamide is then separated from the calcium sulphate, and dicyandiamide formed as a by-product by extraction with ether. The ether is diluted, as another by-product is often precipitated which is not soluble in the dilute solution of cyanamide in ether. After distilling off the ether, pure cyanamide which distils at 143—144°/18 mm., is obtained. On treatment with methyl alcohol and hydrochloric acid, it yields the methyl ether of *iso*carbamide. S. B. S.

Double Thiocyanates of Bivalent Copper and of Cobalt with Organic Bases. J. CALZOLARI (*Ber.*, 1910, **43**, 2217—2219).—Cupric thiocyanate, although insoluble in, and decomposed by, water, dissolves unchanged in concentrated solutions of an alkali thiocyanate. From the solution, however, thiocyanates of bivalent copper cannot be isolated, since they readily decompose, especially on warming, with the deposition of cuprous thiocyanate. The following double thiocyanates of bivalent copper with organic bases can, however, be readily isolated.

Tripyridinium cupric thiocyanate, $Cu(CNS)_2,3Py,HCNS$, is obtained as a reddish-brown precipitate by adding a concentrated solution of copper nitrate to a saturated solution of ammonium thiocyanate until the black precipitate first formed redissolves, filtering, and then adding a concentrated solution of pyridine thiocyanate.

Dihexamethylenetetramine cupric thiocyanate,

$$Cu(CNS)_2,2C_6H_{12}N_4,HCNS,$$

separates as a light green, crystalline precipitate when hexamethylenetetramine thiocyanate is used instead of pyridine thiocyanate. Since the compound is anhydrous, the green colour, which is different from the reddish-brown colour of the solutions of cupric thiocyanate in concentrated solutions of the alkali thiocyanates, must depend on the organic base. This is confirmed by the fact that *dihexamethylenetetramine cobalt thiocyanate*, $Co(CNS)_2,2C_6H_{12}N_4,HCNS$, which was prepared in a similar manner to the corresponding copper compound, forms lilac-coloured crystals, whereas the thiocyanates of cobalt are blue.

Hexamethylenetetramine thiocyanate is precipitated from a saturated solution of ammonium thiocyanate (1 mol.) and hexamethylenetetramine (1 mol.) on the addition of hydrogen chloride; it forms large, transparent, colourless, monoclinic prisms. T. S. P.

Crystallographical and Optical Investigations of Organic Compounds. C. BLASS (*Zeitsch. Kryst. Min.*, 1910, **48**, 20—44).—The following crystallographic determinations are given: Potassium

molybdenum hexathiocyanate, pseudohexagonal [$a:c=1:0{\cdot}67197$]; the ammonium salt, rhombic [$a:b:c=0{\cdot}60721:1:0{\cdot}88406$], and the sodium salt, triclinic [$b:c=1:0{\cdot}98114$]. Potassium chromihexathiocyanate, pseudohexagonal [$a:c=1:0{\cdot}67934$], the ammonium salt, rhombic [$a:b:c=0{\cdot}61109:1:0{\cdot}87651$], and the sodium salt, triclinic.

Corydine is tetragonal trapezohedric [$a:c=1:0{\cdot}39896$], and has $[\alpha]_D^{20}$ $+204{\cdot}35°$ in chloroform; bulbocapnine, rhombic hemihedral [$a:b:c=0{\cdot}72520:1:0{\cdot}71792$], $[\alpha]_D^{20}$ $+237{\cdot}1°$ in chloroform; bulbocapnine monomethyl ether, tetragonal hemihedral [$a:c=1:1{\cdot}05540$], $[\alpha]_D^{20}$ $+247{\cdot}2°$ in chloroform; monobenzoylbulbocapnine, rhombic [$a:b:c=0{\cdot}89437:1:0{\cdot}63116$], $[\alpha]_D^{20}$ $+92{\cdot}7°$ in chloroform; ephedrinephenylthiocarbamide, rhombic hemihedral sphenoidal [$a:b:c=0{\cdot}81703:1:0{\cdot}42834$], $[\alpha]_D^{20}$ $-105{\cdot}1°$ in abs. alcohol; ψ-ephedrinethiocarbamide, rhombic [$a:b:c=0{\cdot}37134:1:0{\cdot}62669$], $[\alpha]_D^{20}$ $+22{\cdot}8°$ in absolute alcohol.

Patchouli-alcohol, hexagonal [$a:c=1:0{\cdot}56528$], $[\alpha]_D^{20}$ $-124{\cdot}5°$ in alcohol; cedrol, rhombic [$a:b:c=0{\cdot}98385:1:0{\cdot}70502$], $[\alpha]_D^{20}$ $-84°$ to $-61°$; cypress camphor, rhombic [$a:b:c=0{\cdot}98844:1:0{\cdot}71772$], is optically inactive; guaiol (champacol), trigonal pyramidal [$a:c=1:0{\cdot}54959$], $[\alpha]_D$ $-29{\cdot}8°$; benzoyleugenol, monoclinic [$a:b:c=1{\cdot}5829:1:1{\cdot}0713$]; acetyl*iso*eugenol, rhombic [$a:b:c=0{\cdot}68815:1:0{\cdot}97672$]; *iso*apiole, monoclinic [$a:b:c=0{\cdot}876502:1:1{\cdot}7878$]; menthyl benzoate, rhombic [$a:b:c=0{\cdot}76134:1:0{\cdot}24476$], $[\alpha]_D^{20}$ $-90{\cdot}72°$; guaiolglycerol, rhombic [$a:b:c=0{\cdot}23916:1$].

α'-Methyl-α-ethylolpiperidine, rhombic [$a:b:c=0{\cdot}6777:1:0{\cdot}61179$].

T. S. P.

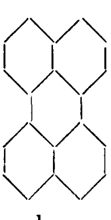
The Destruction of Cyanide. JAMES MOIR and JAMES GRAY (*Chem. Met. Min. Soc. S.A.*, 1910, **10**, 433—441).—Experiments are described which had for their object the destruction of cyanide. Complete destruction can be achieved by several methods (such as the action of silver and cuprous salts and of ammonium disulphide), but the ferrocyanide reaction is the only one which would be commercially successful on the Rand. A thorough investigation of this reaction showed (1) that when *excess* of alkali is used, the amount of ferrocyanide formed is less than when smaller quantities of alkali are present; (2) that rise of temperature above 20° is harmful to the reaction; (3) that the results are nearly independent of dilution; (4) that the reaction is as complete in five to ten seconds as after a long time, and (5) that unless the alkalinity is most carefully adjusted to suit the amount of iron used, an excess of ferrous solution gives no better results than the theoretical quantity (that required by the equation: $6KCN + 2FeSO_4,7H_2O = K_2Fe[Fe(CN)_6] + 2K_2SO_4 + 7H_2O$).

In no case have the authors succeeded in obtaining entire destruction of the cyanide used, although in several cases they obtained a reaction sufficiently complete for all industrial purposes, the cyanide having been reduced to three or four parts per million.

It is pointed out that a solution containing free hydrocyanic acid cannot be correctly estimated with silver nitrate; for correct results it is necessary to add an excess of alkali before titration with the silver nitrate.

T. S. P.

Perylene, a Highly Condensed Aromatic Hydrocarbon, $C_{20}H_{12}$. ROLAND SCHOLL, CHRISTIAN SEER, and RICHARD WEITZENBÖCK (*Ber.*, 1910, **43**, 2202—2209).—Scholl and Mansfeld (this vol., i, 494) have shown that *meso*-benzdianthrone, when heated at 140—145° with anhydrous aluminium chloride, is converted into *meso*-naphthadianthrone. By the same reaction the hydrocarbon $C_{20}H_{12}$ (annexed formula) is obtained from 1 : 1′-dinaphthyl and also directly from naphthalene. To establish the constitution as a *peri*-derivative, 1 : 8-naphthalenediamine was converted into the azimide, this into 8-*iodo-α-naphthylamine*, and further into 1 : 8-*di-iodonaphthalene*, which last when heated with copper powder yielded the above hydrocarbon, peri-*dinaphthalene*, which it is proposed to term perylene. *Perylene* forms glistening yellow or bronze-hued, crystalline plates, m. p. 264—265°, and gives yellow or reddish-yellow solutions with a brilliant blue fluorescence.



8-*Iodo-α-naphthylamine* forms colourless needles, m. p. 82°; the *hydrochloride* forms grey needles, which darken at 170°, m. p. 186—189° (decomp.). 1 : 8-Di-iodonaphthalene forms bright brown needles, m. p. 109°.

Dibenzoylperylene, prepared by the action of benzoyl chloride and aluminium chloride on perylene, was obtained in yellow crystals, m. p. 280—285°; the xylene solution shows a green fluorescence.

E. F. A.

Monoalkylnitroamines. ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], 14, 296—312. Compare Abstr., 1898, i, 9).—Contrary to the observations of Simon Thomas (Abstr., 1891, 167), the author finds that picryl chloride in alcoholic solution reacts with the potassium salts of ethyl- and propyl-nitroamine, giving respectively trinitrophenyl-ethyl- and -propyl-nitroamines. The yield of trinitrophenylethylnitroamine amounts to almost 90% of theory, but in the second reaction only about two-thirds of the picryl chloride is decomposed, a mixture of almost equimolecular quantities of potassium chloride and picrate being precipitated, whilst the unattacked picryl chloride will react with a further amount of potassium propylnitroamine. Similarly, potassium butylnitroamine when treated with picryl chloride gives a small quantity of *trinitrophenylbutylnitroamine*, $C_4H_9{\cdot}N(NO_2){\cdot}C_6H_2(NO_2)_3$, which forms almost colourless, nacreous spangles, m. p. 98—99°, together with much potassium picrate.

This compound can also be prepared by van Romburgh's method (*Rec. trav. chim.*, 1883, **2**, 112), *trinitrophenylbutylamine*,

$$C_4H_9{\cdot}NH{\cdot}C_6H_2(NO_2)_3,$$

which crystallises in long, slender, orange-yellow needles, m. p. 80·5—81°, being an intermediate product.

The decreasing yield of aliphatic trinitrophenylnitroamine, obtained on ascending the series of aliphatic nitroamines, is probably due to the increasing degree of dissociation of the potassium salts of the latter, and thus supports Simon Thomas's conclusion that methylnitroamine has a more strongly acid character than that possessed by its homologues.

Attempts to prepare acetyl or benzoyl derivatives of methylnitroamine failed (compare Simon Thomas, *loc. cit.*). With benzoyl chloride alone, or in the presence of benzene, methylnitroamine gives nitrous oxide, methyl chloride, and benzoic acid. Addition of benzoyl chloride to a mixture of the silver derivative of methylnitroamine with sand causes a violent explosion. The reaction with benzoyl chloride is explicable on the assumption that methylnitroamine has the constitution

$$NMe\colon NO\cdot OH.$$

The nitroamine is perhaps transformed into the latter under the influence of substances with which it reacts, thus the salts of *o*- and *p*-nitrophenol and of carbonic, hydrocyanic, cyanic, sulphydric, sulphurous, and nitrous acids are decomposed by it, but it does not combine directly with aromatic amines, although it does so with ammonia. This constitution is also supported by the observation that methylnitroamine combines with piperidinomethyl alcohol and with piperazine. In the former case, large, colourless crystals, m. p. 52°, of *piperidinemethylnitroaminomethane*, $NO_2\cdot NMe\cdot CH_2\cdot C_5NH_{10}$, are produced. This compound is unstable, and dissolves slowly with decomposition in cold water. Butylnitroamine reacts with piperidinomethyl alcohol, giving a *liquid product*, whilst ethylenedinitroamine forms magnificent crystals, m. p. 123°, of *piperidine-ethylenedinitroaminomethane*, $C_2H_4[N(NO_2)\cdot CH_2\cdot C_5NH_{10}]_2$, which behave similarly to the methyl derivative. With piperazine, methylnitroamine forms *piperazinedimethylenedinitroamine*,

$$NO_2\cdot NMe\cdot CH_2\cdot N{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}N\cdot CH_2\cdot NMe\cdot NO_2,$$

which crystallises in nacreous leaflets, decomposing at 170°.

The latter compounds react as though they possess the constitution $R\cdot N\colon NO\cdot OR'$; nevertheless, in previous communications (Abstr., 1899, i, 106), reactions in support of the formula $CH_3\cdot NH\cdot NO_2$ for methylnitroamine have been described. E. H.

Trinitrophenylalkylnitroamines. ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], **14**, 313—314).—The alkylpicramides, $C_6H_2(NO_2)_3\cdot NHR$, are yellow or orange-coloured substances, whilst the trinitrophenylalkylnitroamines are only very faint yellow, but are coloured purple-red by alkalis.

The author considers that the difference in colour between the two classes of compounds is related to the replacement of the imide hydrogen by the nitro-group, and points out that this is in accordance with the views recently expressed by Hantzsch (this vol., i, 475). The coloration of the trinitrophenylalkylnitroamines by alkalis is perhaps due to the conjugation of two nitro-groups with the metal or ammonia (compare Hantzsch and Picton, Abstr., 1909, i, 467).

E. H.

Homochromoisomerism. MAX BUSCH (*Ber.*, 1910, **43**, 2070. Compare Hantzsch, this vol., i, 474).—Polemical. Busch and Pungs (Abstr., 1909, i, 564) were the first to recognise the two isomerides of picrylmethylaniline, and to carry out the mutual interconversion.

E. F. A.

Products of the Bromination of *o*- and *p*-Nitrophenol. HENRI VAN ERP (*Rec. trav. chim.*, 1910, [ii], **14**, 187—237).—The author has studied the preparation of 4-bromo-, 6-bromo- and 4 : 6-dibromo-2-nitrophenol, 2-bromo- and 2 : 6-dibromo-4-nitrophenol, 4-bromo-2 : 6-dinitrophenol, and 2-bromo-4 : 6-dinitrophenol. A résumé of the literature relative to each of these compounds is given. The following new compounds are described. *Calcium 4-bromo-2-nitrophenoxide*, $(C_6H_3O_3NBr)_2Ca,2H_2O$, forms a bright orange precipitate composed of microscopic needles ; *4-bromo-2-nitrophenyl acetate*, prepared from the phenol by means of acetic anhydride containing a small quantity of sulphuric acid, crystallises in very brilliant, colourless, triangular plates, m. p. 74·5—74·75°. By treating the product of the bromination of *o*-nitrophenol with aniline, the author separated a small quantity of 6-bromo-2-nitrophenol, which has not hitherto been prepared in this way. *Barium 4 : 6-dibromo-2-nitrophenoxide*, $(C_6H_2O_3NBr_2)_2Ba,2H_2O$, forms thin, doubly-refracting, orange needles ; the *additive* compound of 4 : 6-dibromo-2-nitrophenol and aniline, $NO_2\cdot C_6H_2Br_2\cdot OH,NH_2Ph$, a crystalline, yellow powder, m. p. 87° (variable), easily breaks down into its components. If 4 : 6-dibromo-2-nitrophenol is left in contact with nitric acid (D 1·41) for some months, it is converted into 2-bromo-4 : 6-dinitrophenol, of which the *aniline* derivative has m. p. 151°. For 4-bromo-2 : 6-dinitrophenol the author finds m. p. 74·5°, whilst Körner (*Zeit. Chem.*, 1868, **4**, 322) and Armstrong and Prevost (Trans., 1875, **28**, 520 ; Abstr., 1874, 1164) give 78°, and Austen (*Jahresber*, 1878, i, 550) gives 71°.

Potassium 4-bromo-2 : 6-dinitrophenoxide, $C_6H_2O_5N_2BrK$, is a blood-red substance ; the *sodium* salt, $C_6H_2O_5N_2BrNa,2H_2O$, forms thin, doubly-refracting needles of the same colour ; the *barium* and *calcium* salts, $(C_6H_2O_5N_2Br)_2Ca,2H_2O$, crystallise in bright yellow needles. The *additive* compound of 4-bromo-2 : 6-dinitrophenol and aniline, $C_6H_3O_5N_2Br,PhNH_2$, is an orange, microcrystalline powder, m. p. 137·5—137·75°, sufficiently stable to be recrystallised from warm water ; *4-bromo-2 : 6-dinitrophenyl acetate* crystallises in brilliant doubly-refracting, colourless, orthorhombic prisms, m. p. 110·5°, which become yellowish-brown in moist air.

By the bromination of *p*-nitrophenol, previous workers have obtained 2-bromo-4-nitrophenol with too low a m. p. (102°). This is shown to be due to admixture with dibromonitrophenol, which cannot be removed by recrystallisation of the phenol or of its barium or potassium salt. By treating the benzene solution of the bromination product with aniline, the dibromonitrophenol is precipitated in the form of its aniline derivative. Pure 2-bromo-4-nitrophenol can be obtained from the filtrate in crystals, m. p. 112·25°. The presence of hydrobromic acid inhibits the formation of the dibromo-compound to a certain extent. *Sodium 2-bromo-4-nitrophenoxide*,

$$C_6H_3O_3NBrNa,2H_2O,$$

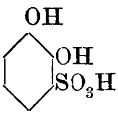
and the *potassium* salt ($1\frac{1}{2}H_2O$) crystallise in radial groups of microscopic, bright yellow, doubly-refracting, pointed needles ; the *calcium* salt forms a microcrystalline powder composed of thin needles ; the *additive* compound of 2-bromo-4-nitrophenol and aniline,

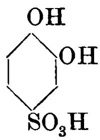
$$C_6H_4O_3NBr,NH_2Ph,$$

forms greenish-yellow crystals, m. p. 55—69°, which lose aniline

completely when exposed over sulphuric acid in a vacuum; *2-bromo-4-nitrophenyl acetate* crystallises in irregular, birefracting, colourless prisms, m. p. 61·75°. For 2:6-dibromo-4-nitrophenol the author observed the m. p. 143°, and, contrary to the statements of previous workers, found that it was not decomposed at 180°. *Sodium 2:6-dibromo-4-nitrophenoxide*, $C_6H_2O_3NBr_2Na$, crystallises above 50° with $2H_2O$ in deep orange crystals, and below 20° with $5H_2O$ in yellow crystals; the *calcium* salt, $(C_6H_2O_3NBr_2)_2Ca,4H_2O$, crystallises in irregular, doubly-refracting, orange-coloured rhombs; the *additive* compound of 2:6-dibromo-4-nitrophenol and aniline, $C_6H_3O_3NBr_2,NH_2Ph$, forms slender, yellow needles, m. p. 155·5°, which give almost colourless solutions in neutral solvents and only lose aniline very slowly when boiled with water. *Potassium 2-bromo-4:6-dinitrophenoxide* crystallises with $1H_2O$; the *additive* compound of 2-bromo-4:6-dinitrophenol and aniline, $C_6H_3O_5N_2Br,NH_2Ph$, forms slender, yellow needles, m. p. 151°, and can be recrystallised from boiling water; *2-bromo-4:6-dinitrophenyl acetate* forms short, stout, doubly-refracting, colourless, rhombohedric crystals, m. p. 104·5° E. H.

Catecholmonosulphonic Acid. CURT GENTSCH (*Ber.*, 1910, **43**, 2018—2020).—Cousin (Abstr., 1893, i, 637) considered the catecholsulphonic acid, which he obtained by sulphonating catechol below 100°, to be an ortho-acid of constitution (I), and isomeric with the para-acid (II) described by Barth (Abstr., 1879, 933).


(I.)


(II.)

It is shown that the two acids are identical, both forming a characteristic barium salt ($4H_2O$) crystallising in rosettes of rectangular prisms, whilst Cousin's acid gives 1:2-dimethoxybenzene-4-sulphonic acid (compare Paul, Abstr., 1906, i, 843) on methylation. It must accordingly be removed from the literature. E. F. A.

Simple Formation of Benzyl Ethers. HANS VON HALBAN (*Ber.*, 1910, **43**, 2071. Compare Braun, this vol., i, 479).—Polemical. The fact that benzyl halogenides react with alcohol, forming ethers, has already been observed (compare Abstr., 1909, ii, 722). Benzyl halogenides also react with phenols and carboxylic acids.

E. F. A.

Preparation of Aromatic Alcohols and their Acetates. ALFRED WOHL and ERICH BERTHOLD (*Ber.*, 1910, **43**, 2175—2185).—Grignard (Abstr., 1904, i, 494) has described the preparation of phenylethyl alcohol by the following series of reactions:

$$CH_2Br\cdot CH_2Br \longrightarrow CH_2Br\cdot CH_2\cdot OPh,$$
$$CH_2Ph\cdot CH_2\cdot OPh \longrightarrow CH_2Ph\cdot CH_2Br \longrightarrow CH_2Ph\cdot CH_2\cdot OH,$$

and the authors have re-examined these reactions in detail. A 59% yield of pure ω-bromophenetole can be obtained by gradually adding 4*N*-sodium hydroxide solution to a mixture of ethylene dibromide, phenol, and water heated in an oil-bath at 100—105°, and kept well stirred. A 48·4% of ω-chlorophenetole can be obtained by a similar method, using ethylene dichloride, a shaking apparatus, and a tem-

perature of 110°. β-Naphthol gives a 40% yield of its ω-bromoethyl ether (Kolbe, Abstr., 1881, 177). Eugenole gives a 25% yield of the *bromoethyl ether*, $CH_2:CH\cdot CH_2\cdot C_6H_3(OMe)\cdot O\cdot CH_2\cdot CH_2Br$, which has m. p. 26—27° and b. p. 160—170°/7 mm.

Guaiacol ω-bromoethyl ether, $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2Br$ (40% yield), has m. p. 43—45° and b. p. 135—140°/7 mm.

Phenyl vinyl ether, $CH_2:CH\cdot OPh$, obtained by heating ω-bromophenetole with twice its weight of anhydrous potassium hydroxide in a copper flask, is a colourless liquid, b. p. 155—156°. A by-product is *diphenoxyethyl ether*, $O(CH_2\cdot CH_2\cdot OPh)_2$, which crystallises from dilute alcohol in colourless needles, m. p. 66—67°. *Eugenyl vinyl ether*, $CH_2:CH\cdot CH_2\cdot C_6H_3(OMe)\cdot O\cdot CH_2:CH_2$ (50% yield), is a mobile liquid, b. p. 260—262°, and *guaiacyl vinyl ether* (50% yield) has b. p. 202—203°.

ω-Bromophenetole, bromobenzene, and sodium powder in the presence of ether yield phenol, ethylene, and unaltered bromobenzene.

A 71% yield of ω-phenylphenetole is obtained by the action of magnesium phenyl bromide on ω-bromophenetole in the presence of xylene at 150—155°, and when this is boiled with glacial acetic acid and 70% sulphuric acid, a 65% yield of phenylethyl acetate is obtained.

A 38% yield of phenylethyl alcohol can be obtained by the action of nitrous acid on β-phenylethylamine.

Phenylmethylvinyl acetate, $CMePh:CH\cdot OAc$, obtained by boiling hydratropaldehyde with acetic anhydride and two drops of concentrated sulphuric acid, is a clear, colourless liquid, b. p. 120—122°/8—9 mm., and when reduced with hydrogen and platinum black yields *β-phenylpropyl acetate*, $CHMePh\cdot CH_2\cdot OAc$, with b. p. 103—105°/10 mm.

J. J. S.

Fixation of Trioxymethylene by Magnesium Derivatives of the Homologues of Benzyl Bromide. PAUL CARRÉ (*Compt. rend.*, 1910, **151**, 149—151.* Compare Abstr., 1909, i, 544).—Trioxymethylene reacts with magnesium mesityl bromide in the same way as with magnesium benzyl chloride (Tiffeneau, Abstr., 1904, i, 48), forming *s*-mesitylcarbinol, $C_6H_3Me_2\cdot CH_2\cdot OH$, needles, m. p. 88—89°, b. p. 140—141°/15 mm.; the *phenylurethane* crystallises in long prisms, m. p. 124—125°. The product of the reaction also contains *s*-dixylylethane (Moritz, Abstr., 1899, i, 910), mesitylene, and *s-dixylyldimethyl ether*, $O(CH_2\cdot C_6H_2Me_2)_2$, silky needles, m. p. 148°. The constitution of the latter follows from its conversion by hydrogen bromide into *2:4:6-trimethylbenzyl bromide*, $C_6H_2Me_3\cdot CH_2Br$, long tablets, m. p. 52°, which yield *s*-mesitylcarbinol on hydrolysis.

Wispek's *s*-xylylacetic acid has m. p. 103° (Abstr., 1883, 1095); it could not be detected amongst the products of the foregoing reaction. The *ethyl* ester has b. p. 141—142°/18 mm., and on reduction forms *s-xylylethanol*, a mobile liquid having a rose-like odour, b. p. 134—135°/15 mm.; the *phenylurethane* crystallises in long prisms, m. p. 99°; the *acetate* has b. p. 138—139°/13 mm.

W. O. W.

Crystalline Form of Cholesteryl Salicylate. ETTORE ARTINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 782—784).—Cholesteryl

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 841—846.

salicylate, $OH\cdot C_6H_4\cdot CO_2\cdot C_{27}H_{45}$, prepared by fusing cholesterol and salicylic acid at 170°, melts at 180°, and has $[\alpha]_D^{15}$ $-53\cdot78°$ in chloroform solution. The crystals are small, but distinctly formed, and are triclinic [$a:b:c=0\cdot77364:1:0\cdot50407$; $\alpha=92°55'24''$, $\beta=101°58'32''$, $\gamma=95°14'10''$]. C. H. D.

pp-**Dibromobenzhydrol. A Correction.** HEINRICH BILTZ (*Ber.*, 1910, **43**, 2262. Compare this vol., i, 570).—The compound, m. p. 174—175°, obtained by the decomposition of dibromobenzilic acid, and described as dibromobenzhydrol, is in reality di-*p*-bromobenzophenone. E. F. A.

Condensation of Ethyl Nitrate with *o*-**Bromophenylacetonitrile.** WILHELM WISLICENUS and MAX FISCHER (*Ber.*, 1910, **43**, 2234—2243).—Ethyl nitrate condenses with *o*-bromophenylacetonitrile in presence of sodium ethoxide less readily than with the corresponding *p*-compound (Abstr., 1909, i, 29). In presence of potassium ethoxide the *potassium* salt of o-*bromo-α-*iso*nitrophenylacetonitrile*, $C_6H_4Br\cdot C(CN):NO_2K$, is obtained. Nitrous acid is readily eliminated from the free compound to form oo'-*dibromo-αα'-dicyanostilbene.* The *iso*nitro-group is more stable in alkaline solution; on boiling, cyanide is eliminated and o-*bromo-ω-nitrotoluene* formed. Stronger heating causes the elimination of the oximino-group also, and oo'-*dibromostilbene* is obtained. Sodium hydroxide and hydrogen peroxide convert the cyano-group into carbonamide. Treatment with bromine and subsequent elimination of nitric oxide and bromine leads to *o*-bromophenylacetonitrile. On reduction, *o*-bromo-α-aminophenylacetic acid is obtained.

o-Bromophenylacetonitrile boils without decomp. at 145—147°/13 mm.

Sodium o-*bromo-α-*iso*nitrophenylacetonitrile* crystallises in colourless plates, m. p. 283—285° (decomp.), and explodes on further heating. The *potassium* salt forms colourless, glistening plates. Both salts dissolve in water with a neutral reaction, the solution having a sweet taste. It gives neither coloration nor precipitate with ferric chloride, but the alcoholic solution becomes a deep brownish-red with this reagent.

The free o-*bromo-α-*iso*nitrophenylacetonitrile* forms faintly yellow-coloured, pyramidal prisms, m. p. 51—52°, and gives an intense red coloration with ferric chloride in alcoholic solution. The *methyl ether* is colourless, m. p. 104—105°.

oo'-*Dibromo-αα'-dicyanostilbene*, $[C_6H_4Br\cdot C(CN):]_2$, crystallises in colourless needles, m. p. 145°.

o-*Bromo-ω-nitrotoluene* crystallises in colourless needles, m. p. 55—56°, and shows no ferric chloride reaction.

oo'-*Dibromostilbene* is obtained in colourless, lustrous plates, m. p. 206—208°; the *dibromide* forms colourless needles, m. p. 225°.

o-Bromophenylacetonitrile was obtained in almost colourless, long, flat, glistening needles, m. p. 65—67° (Russanoff: 62—64°). It reacts in ethereal solution with phenylhydrazine, forming o-*bromobenzophenylhydrazide*, which crystallises in needles, m. p. 190—198°.

o-*Bromo-a-aminophenylacetic acid*, $C_6H_4Br\cdot CH(NH_2)\cdot CO_2H$, separates in leaflets, which sublime at 220—225°, m. p. 221° (in closed tube).

The *potassium* salt of o-*bromo-a*-iso*nitrophenylacetamide*,

$$C_6H_4Br\cdot C(CO\cdot NH_2):NO_2K,$$

crystallises in long, faintly yellow-coloured needles, decomp. 240°. On treatment with bromine, *a*:o-*dibromo-a-nitrophenylacetamide* is produced in colourless, microscopic prisms, m. p. 156—157° (decomp.).

E. F. A.

Action of Benzaldehyde on the Monosodium Derivative of Phenylacetonitrile. F. Bodroux and Felix Taboury (*Bull. Soc. chim.*, 1910, [iv], 7, 735—736).—When the monosodium derivative of phenylacetonitrile in ethereal solution is treated with benzaldehyde, the product consists of a mixture of substances. From the latter the only definite compound that can be isolated is α-phenylcinnamonitrile, CHPh:CPh·CN, already described by Meyer, Janssen, Neure, and Frost (Abstr., 1889, 596, 597).

The nitrile is probably formed by the reactions: Ph·CHO + Ph·CHNa·CN = Ph·CH(ONa)·CHPh·CN ; Ph·CH(ONa)·CHPh·CN = NaOH + CHPh:CPh·CN. Sodium benzoate, formed probably by a secondary reaction, is found in the aqueous liquor from which the above crude product is separated. E. H.

The Walden Inversion. V. Optically Active β-Amino-β-phenylpropionic Acid. Emil Fischer, Helmuth Scheibler, and Reinhart Groh (*Ber.*, 1910, **43**, 2020—2030. Compare Abstr., 1909, i, 359).—The formyl compound of β-amino-β-phenylpropionic acid has been resolved by means of quinidine and quinine into the optically active forms. By treatment with nitrous acid, these were converted into the corresponding hydroxy-acids, but the change is accompanied by racemisation, due to the influence of the direct attachment of the phenyl to the asymmetric carbon atom. Enough activity remains, however, to identify the hydroxy-acids with those obtained by McKenzie and Humphries (Trans., 1910, **97**, 121). *d*-β-Amino-β-phenylpropionic acid gives *l*-β-hydroxy-β-phenylpropionic acid. In the case of the ethyl ester of the amino-acid, the racemisation is less, and the hydroxy-acid rotates in the same direction, so that no Walden change takes place.

dl-β-*Formylamino-β-phenylpropionic acid*,

$$CHO\cdot NH\cdot CHPh\cdot CH_2\cdot CO_2H,$$

forms large, colourless prisms, which soften at 125°, m. p. 128—129° (corr.), to a colourless liquid. By means of the *quinidine* salt, d-β-*formylamino-β-phenylpropionic acid* was obtained in aggregates of microscopic, short needles, which soften at 138°, m. p. 142—143°, $[\alpha]_D^{20}$ +116·4° (±0·2°). The *quinine* salt yields the corresponding *l*-isomeride, which is very similar; $[\alpha]_D^{20}$ −114·4° (±0·2°). d-β-*Amino-β-phenylpropionic acid*, obtained by heating the formyl compound with 10% hydrochloric acid, crystallises in stout plates, m. p. 234—235° (decomp.), and has $[\alpha]_D^{20}$ +6·9° in water, −1·3° in *N*-hydrochloric acid, −9·1° in *N*-sodium hydroxide. The l-*isomeride* is precisely similar in crystalline form, and has $[\alpha]_D^{25}$ −7·5° in water, +1·3° in *N*-hydrochloric acid, +8·9° in *N*-sodium hydroxide. The copper salt crystallises in plates.

Ethyl d-*β-amino-β-phenylpropionate* is a viscid oil, b. p. 155° (corr.)/ 13 mm., D_4^{24} 1·063, $[\alpha]_D^{24}$ +13·74° (±0·02°). The *l*-isomeride was prepared from partially racemised material, and had $[\alpha]_D^{20}$ −8·09° (±0·04°).

Conversion of the *d*-*β*-aminophenylpropionic acid into the hydroxy-acid gave a product, m. p. 96—98°; $[\alpha]_D^{25}$ −3·3°, whereas McKenzie and Humphries (*loc. cit.*) found $[\alpha]_D^{20}$ −18·9°. Similarly, the *l*-acid yields an hydroxy-acid; m. p. 94—95°; $[\alpha]_D^{26}$ +3·2°.

Ethyl *d*-*β*-aminophenylpropionate yields the hydroxy-acid; $[\alpha]_D^{22}$ −3·5°, rising to −6·4° on crystallisation. E. F. A.

Action of Esters of Monobasic Aliphatic Acids on the Sodium Derivative of Phenylacetonitrile. F. BODROUX (*Compt. rend.*, 1910, **151**, 234—236.* Compare Walther and Schickler, Abstr., 1897, i, 522).—Sodamide was added to phenylacetonitrile dissolved in dry ether, and an alkyl ester added to the resulting sodium derivative. The following compounds were prepared in this way: *a-Cyanophenylacetaldehyde*, CN·CHPh·CHO, m. p. 157—158°, from ethyl formate, which on benzoylation gave Walther's enolic benzoyl derivative, m. p. 119°. Amyl formate gave the same compound in diminished yield (50%). Ethyl acetate formed *a-cyanobenzyl methyl ketone*, CN·CHPh·COMe, large prisms, m. p. 90°. *a*-Cyano-*a*-phenylbutan-*β*-one has m. p. 73° (Walther and Schickler give m. p. 58°). The foregoing compounds are easily hydrolysed by dilute alkalis, regenerating phenylacetonitrile.

W. O. W.

Tetrahydroellagic Acid. MAXIMILIAN NIERENSTEIN (*Ber.*, 1910, **43**, 2016—2017. Compare this vol., i, 389).—The tetrahydroellagic acid described by Oser and Böker (Abstr., 1880, 394), crystallising from pyridine in small, yellow needles, is in reality ellagic acid.

The isomeric tetrahydroellagic acid of Oser and Kalmann (Abstr., 1881, 815), obtained in small, silky needles by fusing ellagic acid with potassium hydroxide, is in reality pentahydroxydiphenylmethylolide, $C_{13}H_8O_7$. E. F. A.

The Beckmann Rearrangement. PIETER J. MONTAGNE (*Ber.*, 1910, **43**, 2014—2016).—Schroeter (Abstr., 1909, i, 617) has explained the Beckmann rearrangement on the assumption of the formation of an additive product with hydrogen chloride, and the conversion of this into a compound with a univalent nitrogen atom, $R_2CCl{\cdot}N<$. It is pointed out that in the case of the ketoximes, RR′C:N·OH, the additive product and the unsaturated compound cannot be intermediate compounds. Wallach (Abstr., 1906, i, 522) has assumed the elimination and subsequent addition of hydrogen chloride. If this were so, the benzene nucleus, after the rearrangement, must be combined with a different carbon atom than before, which was shown not to be the case (compare Montagne, Abstr., 1907, i, 140, 854). E. F. A.

Isomerism and Polymorphism. I. Ketones of the Type of Benzylidenedeoxybenzoin and their Interconversion by Heat, Light, and Other Agencies. HANS STOBBE and FORSYTH J. WILSON (*Annalen*, 1910, **374**, 237—287).—The isomerism of the benzylidene-

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 848—852.

deoxybenzoins described by Stobbe and Niedenzu (Abstr., 1902, i, 103) has been more thoroughly studied in the cases of the ketones obtained from the three nitrobenzaldehydes and from piperonal.

Hydrogen chloride is passed for six hours into an ethereal solution of deoxybenzoin and *o*-nitrobenzaldehyde at 0°; after being kept for three days at this temperature, the solution deposits white and yellow crystals. The former, after recrystallisation from benzene, have m. p. 132—133°, and consist of *chloro*-o-*nitrobenzyldeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHPh \cdot COPh$, which is an unstable substance, being converted into the *ether*, $NO_2 \cdot C_6H_4 \cdot CH(OEt) \cdot CHPh \cdot COPh$, m. p. 128—129°, by boiling alcohol, and losing hydrogen chloride by keeping in the air or in benzene or ethereal solution, or, best, by heating with aniline, yielding the yellow crystals, which consist of o-*nitrobenzylidenedeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CH{:}CPh \cdot COPh$, m. p. 120—121°. This unsaturated ketone is converted into a paler yellow isomeride, iso-o-*nitrobenzylidenedeoxybenzoin*, m. p. 109—110°, by an exposure to sunlight for three months of its benzene solution containing a little iodine, by passing hydrogen chloride into its benzene solution for a few minutes, and then keeping for eleven hours, or by the action of sunlight on the powdered crystals; in each case a mixture of the two isomerides is produced, which is separated by means of alcohol. The *iso*-compound is more easily converted into the other, the change proceeding to the extent of 50% by exposing its benzene solution containing iodine to sunlight for five days, or by keeping its benzene solution, containing hydrogen chloride, for a week. Both isomerides have the same molecular weight, and yield the same o-*nitrobenzamarone*, $NO_2 \cdot C_6H_4 \cdot CH(CHPh \cdot COPh)_2$, m. p. 237—238°, when their alcoholic solutions are boiled with an equal molecular quantity of deoxybenzoin and a little sodium ethoxide; their alcoholic solutions, however, give different ultraviolet absorption spectra.

When an ethereal mixture of deoxybenzoin and *p*-nitrobenzaldehyde is treated with hydrogen chloride at 0°, and is kept for eleven days, a mixture is obtained, consisting chiefly of stout, yellow prisms of iso-p-*nitrobenzylidenedeoxybenzoin*, m. p. 164—165°, together with smaller amounts of elongated, yellow prisms of allo-p-*nitrobenzylidenedeoxybenzoin*, m. p. 148—149°, and white crystals of *chloro*-p-*nitrobenzyldeoxybenzoin*, $NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHPh \cdot COPh$, m. p. 157—158°, the three substances being separated by fractional crystallisation from alcohol; the last-mentioned compound is converted into a mixture of the other two by boiling 50% potassium hydroxide.

p-*Nitrobenzylidenedeoxybenzoin*, m. p. 133·5—135·5°, which crystallises in yellow prisms, is produced when a benzene solution (containing iodine) of the *iso*-compound is boiled for twelve hours in diffuse daylight. *p*-Nitrobenzylidenedeoxybenzoin and the *iso*- and *allo*-isomerides all have the same molecular weight, yield the same *dibromide*, $NO_2 \cdot C_6H_4 \cdot CHBr \cdot CBrPh \cdot COPh$, decomposing at 156—157°, with bromine in carbon tetrachloride, produce the same p-*nitrobenzamarone*, m. p. 236—237°, and any one is converted into a mixture of the three by (i) exposing its benzene solution, containing iodine, to sunlight for four months, (ii) boiling the same solution for twelve hours in diffuse sunlight,

(iii) keeping its benzene solution, containing hydrogen chloride, for a week. All three give different absorption spectra in alcohol, and also their solutions in concentrated sulphuric acid, or in trichloroacetic acid, are colorimetrically different. A benzene or alcoholic solution of any one, even after being boiled, deposits, on cooling, only crystals of the ketone originally dissolved, even after inoculation with a crystal of either of the other two isomerides. When fused and cooled immediately, any one of the three isomerides resolidifies unchanged, but if kept in the molten condition for only five minutes a change occurs, and a mixture of the three ketones is formed.

The action of hydrogen chloride on an ethereal solution of deoxybenzoin and *m*-nitrobenzaldehyde at 0° leads, after three days, to the formation of a white precipitate, consisting of two stereoisomeric (?) modifications of *a-chloro-*m*-nitrobenzyldeoxybenzoin*,

$$NO_2\cdot C_6H_4\cdot CHCl\cdot CHPh\cdot COPh,$$

which are separated by crystallisation from benzene; one form crystallises in white needles, m. p. 181—182°, the other in stout, white crystals, m. p. 192—193°. When boiled with potassium hydroxide the latter yields *m-nitrobenzylidenedeoxybenzoin*, m. p. 85·5—86·5°, crystallising in white needles, whilst the former yields a mixture of *m*-nitrobenzylidenedeoxybenzoin and iso-*m-nitrobenzylidenedeoxybenzoin*, yellow prisms, m. p. 86·5—87·5°, the two being separated by crystallisation, first from ethyl acetate, and then from alcohol. *m*-Nitrobenzylidenedeoxybenzoin crystallises unchanged from boiling solutions; the *iso*-compound, however, is partly converted into allo-*m-nitrobenzylidenedeoxybenzoin*, m. p. 94·5—95·5°, which crystallises in white prisms. All three isomerides have the same molecular weight, form the same *dibromide*, decomposing at 159—161°, and the same *m-nitrobenzamarone*, m. p. 220—221°, and are mutually interconvertible by boiling their solutions in benzene, containing iodine, in diffuse daylight, by keeping their benzene solutions, containing hydrogen chloride, for a week, or by heating at 160°; by each method a mixture of the three isomerides is produced from any one. The *iso*- and the *allo*-isomerides show almost identical behaviour, giving the same absorption spectra in alcohol, different from that of *m*-nitrobenzylidenedeoxybenzoin, and solutions in concentrated sulphuric acid or trichloroacetic acid, which are colorimetrically the same. Solutions of the *iso*- or of the *allo*-isomeride in any solvent deposit mixtures of both, whilst *m*-nitrobenzylidenedeoxybenzoin alone separates from its solutions, even after inoculation with a crystal of either of the other two isomerides. All three melt and resolidify to the original substance if cooled at once, but when kept in a state of fusion for five minutes, *m*-nitrobenzylidenedeoxybenzoin changes to a mixture of the *iso*- and the *allo*-isomerides, *iso*-*m*-nitrobenzylidenedeoxybenzoin resolidifies unchanged, whilst the *allo*-isomeride partly changes into *m*-nitrobenzylidenedeoxybenzoin. When slowly heated, a mixture of equal parts of *m*-nitrobenzylidenedeoxybenzoin and the *iso*- or *allo*-isomeride fuses at a temperature below the m. p. of either constituent, whilst mixtures of the *iso*- and the *allo*-isomerides have the same m. p. as the *allo*-isomeride.

The action of hydrogen chloride on ethereal piperonal and deoxy-

benzoin at 0° leads, after twelve hours, to the production of a yellow mass, from which *chloropiperonyldeoxybenzoin*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CHCl{\cdot}CHPh{\cdot}COPh,$$

m. p. 167—168° (decomp.), is obtained in colourless crystals by crystallisation from benzene. The substance is converted into the *ethyl ether*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHPh{\cdot}COPh$, m. p. 114—115°, by boiling ethyl alcohol, into the corresponding *methyl ether*, m. p. 119—120°, by boiling methyl alcohol, and by boiling water into a mixture of *piperonylidenedeoxybenzoin*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CPh{\cdot}COPh$, m. p. 128—129°, crystallising in white prisms, and iso*piperonylidenedeoxybenzoin*, m. p. 119—120°, crystallising in yellow prisms. The two isomerides give different absorption spectra. They can be recrystallised unchanged from solvents of low b. p., but either is converted into a mixture of the two by boiling its solution in benzene, containing iodine, in diffused daylight, or by the exposure of the same solution to sunlight at the ordinary temperature.

The nature of the isomerism described above is discussed at some length. There is no doubt that the *iso*- and the *allo*-isomerides resemble each other much more closely than the ketones with unprefixed names. The last and the *iso*-isomerides are most probably *syn*- and *anti*-stereoisomerides. The *iso*- and the *allo*-isomerides undoubtedly differ from each other in solution and in the fused state; they are, therefore, true chemical isomerides, for the representation of which the ordinary formulæ do not suffice. C. S.

Ring Formation from the Ketonic Acids. EDMOND E. BLAISE and A. KOEHLER (*Bull. Soc. chim.*, 1910, [iv], 7, 710—721).—It has been shown previously (Vorländer, Abstr., 1897, i, 272; Blaise and Maire, Abstr., 1908, i, 390) that the δ-ketonic acids are condensed by sodium ethoxide to form derivatives of dihydroresorcinol.

The object of the present work was to determine whether this property persists in the ε-, ζ-, and η-ketonic acids, in which the carbonyl group is farther removed from the carboxyl group in the molecule, and if so, the manner in which the ring-formation is effected.

The esters of the ε-ketonic acids under the above conditions are transformed into 2-acyl*cyclo*pentanones. The fact that the product of the condensation of ethyl ω-acetyl-*n*-valerate contains only one hydrogen atom replaceable by alkyl groups, shows that a heptamethylene derivative is not formed according to such a scheme as $\begin{matrix} CH_2{\cdot}CH_2{\cdot}CO{\cdot}OEt \\ | \\ CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \end{matrix} = \begin{matrix} CH_2{\cdot}CH_2{\cdot}CO \\ | \\ CH_2{\cdot}CH_2{\cdot}CO \end{matrix}{>}CH_2 + EtOH$, and therefore that the reaction differs from that undergone by the δ-ketonic acids. The 2-acyl*cyclo*pentanones, being β-diketones, contain a hydrogen atom replaceable by sodium, the derivatives so formed being readily alkylated. Special precautions, however, are necessary in carrying out this alkylation, otherwise the closed carbon chain is ruptured by the action of the sodium ethoxide. The 2-acyl-2-alkyl*cyclo*pentanones are readily hydrolysed by alkalis, giving δ-alkyl-ε-ketonic acids.

The esters of the ζ-ketonic acids are similarly condensed by sodium

ethoxide, giving 2-alkyl*cyclo*hexanone, not octandione, derivatives, whilst the η-ketonic acids do not undergo ring-formation. The conclusion is drawn that compounds containing more than six carbon atoms in a closed chain cannot be produced by reactions of this kind.

2-Propionyl*cyclo*pentanone, $\begin{array}{l}CH_2\cdot CH(COEt)\\ \vert \\ CH_2\cdot CH_2\text{———}\end{array}\!\!>CO$ (Abstr., 1909, i, 479), gives a violet coloration with ferric chloride; the *copper* salt forms grey leaflets; the *magnesium* salt, needles, m. p. 113—114° (decomp.), which contain $2H_2O$; the *pyrazole* crystallises in hexagonal prisms, m. p. 119°; in acetic acid it has a molecular weight corresponding with the formula $C_8H_{12}N_2$, but in benzene the molecular weight agrees with that of the azine, $C_{16}H_{24}N_4$; the *disemicarbazone* forms a crystalline powder, m. p. 236°.

2-*Propionyl*-2-*methyl*cyclo*pentanone* is a colourless liquid, b. p. 94—96°/12 mm. It gives no coloration with ferric chloride. 2-*Propionyl*-2-*ethyl*cyclo*pentanone* has b. p. 107—108°/12 mm. It gives no coloration with ferric chloride. δ-*Propionyl*-n-*hexoic acid*,

$$COEt\cdot CHMe\cdot[CH_2]_3\cdot CO_2H,$$

is a colourless liquid, b. p. 164°/10 mm.; the *semicarbazone* has m. p. 139·5°. δ-*Propionyl*-n-*heptoic acid*, $CH_2Me\cdot CH(COEt)\cdot[CH_2]_3\cdot CO_2H$, is a colourless liquid, b. p. 177°/11 mm.; the *semicarbazone* forms a white powder, m. p. 158—159°; the p-*nitrophenylhydrazone* forms canary-yellow crystals, m. p. 73° (rapid heating), 83—84° (slow heating); the *ethyl* ester has b. p. 136°/11 mm.

2-Propionyl*cyclo*hexanone (Abstr., 1909, i, 479) is a colourless liquid, having an agreeable odour resembling that of acetophenone; the *copper* salt forms small, greenish-grey crystals; the *carbamido-pyrazole*, $\begin{array}{l}CH_2\cdot CH_2\cdot C\text{———}CEt\\ \vert \qquad\qquad\quad \Vert \\ CH_2\cdot CH_2\cdot C\cdot N(CO\cdot NH_2)\end{array}\!\!>N$ or

$$\begin{array}{l}CH_2\cdot CH_2\cdot C\!:\!CEt\\ \vert \qquad\qquad\quad \vert \\ CH_2\cdot CH_2\cdot C\!=\!=N\end{array}\!\!>N\cdot CO\cdot NH_2,$$

magnificent prisms, m. p. 126—127° (very rapid heating), 118° (slow heating), is formed under the conditions which give rise to the disemicarbazone in the case of the *cyclo*pentanone. When treated with sodium ethoxide and an alkyl iodide, 2-propionyl*cyclo*hexanone gives an inseparable mixture of aliphatic esters. E. H.

Constitution of Fenchone. III. Louis Bouveault and F. Levallois (*Bull. Soc. chim.*, 1910, [iv], 7, 736—740).—It has already been shown (Abstr., 1908, i, 193) that when di*apo*fenchylcarbamide, $CO(NH\cdot C_9H_{17})_2$, is heated with 40% sulphuric acid, an unsaturated hydrocarbon, *apo*fenchene, C_9H_{16}, is formed. An attempt was made to characterise this hydrocarbon by preparing crystalline derivatives, but the additive compounds with hydrogen chloride and bromide and with nitrosyl chloride are liquids. From the product of the action of the nitrosochloride on piperidine, a trace of a *substance*, m. p. 175·5°, which is possibly the nitrolpiperidide, can be isolated. From the fact that, contrary to the original statement, the optical rotatory

power of the hydrocarbon is not constant, the authors conclude that *apo*fenchene is a mixture of the three hydrocarbons:

$$\begin{matrix}CH_2\cdot CH_2 \\ | \\ CMe{:}CH\end{matrix}\!\!>CHPr^{\beta} \qquad \begin{matrix}CH{-}CH_2 \\ \| \\ CMe\cdot CH_2\end{matrix}\!\!>CHPr^{\beta} \qquad \begin{matrix}CH_2{-\!\!-\!\!-}CH_2 \\ | \\ C({:}CH_2)\cdot CH_2\end{matrix}\!\!>CHPr^{\beta}$$

(I.) (II.) (III.)

which are the possible products of decomposition of the amide

$$CO(NH\cdot C_9H_{17})_2.$$

The isomeride (II) is certainly present to a considerable extent, (I) is probably present, and the mixture perhaps contains a small quantity of the (III) isomeride. The objection raised by Schimmel & Co. that a molecular transposition may have occurred during the reaction with sulphuric acid is controverted by the observation that the same hydrocarbon (b. p. 143°) is obtained by the action of nitrous acid on dihydrofencholenamide, $C_9H_{17}\cdot CO\cdot NH_2$.

When an alcoholic solution of *apo*fenchene is saturated with hydrogen chloride, the *hydrochloride*, $C_9H_{17}Cl$, is formed. It is a colourless, agreeably smelling liquid, b. p. 60°/8 mm., D_0^4 0 941, D_0^{18} 0·927, α_D +1·24°. The *hydrobromide*, prepared similarly, is a very unstable substance, b. p. 83°/13 mm., losing hydrogen bromide and becoming black very readily. It is reduced by magnesium to *apo*fenchene. E. H.

Sesquiterpene Alcohols. H. KIMURA (*Ber. Deut. pharm. Ges.*, 1910, **20**, 293—297).—The author has shown previously that liquid *iso*cryptomeriol, by conversion into its xanthate and subsequent decomposition of the ester, is changed into solid cryptomeriol (this vol., i, 53). By similar treatment, cedrol is changed into its solid form, m. p. 86°, but santalol remains liquid, although its rotation is changed from −17°15′ to −5°. Also, the solid form of cedrol is obtained when the alcohol or its potassium derivative is distilled with superheated steam and the distillate is kept for several weeks. C. S.

Oil of Savin. FRITZ ELZE (*Chem. Zeit.*, 1910, **34**, 767—768).—A product can be isolated from oil of savin which is easily soluble in dilute alcohol, and has a more intense odour than the original oil. It has D_{15} 0·960, and α_{100} +68°. On saponification with alcoholic potassium hydroxide and fractional distillation under diminished pressure of the product obtained by steam distillation, sabinol,

$$C_{10}H_{15}\cdot OH,$$

was obtained (D_{15} 0·950 and α_{100} +6°). The acetate prepared from this sabinol had D_{15} 0·972, α_{100} +79°, and b. p. 81—82°/3 mm. The original oil thus consisted mainly of sabinol acetate, about 83%.

The following products were also isolated in the fractional distillation: *n*-decaldehyde, geraniol, and dihydrocuminyl alcohol. T. S. P.

Curcumin. J. MIŁOBĘDZKA, STANISLAUS VON KOSTANECKI, and VICTOR LAMPE (*Ber.*, 1910, **43**, 2163—2170).—Various hydroxychalkones have been synthesised in order to compare them with

curcumin. They resemble this compound, but do not dye unmordanted cotton. Vanillin condenses but slowly with pæonol, yielding 2′ : 4-*dihydroxy*-4′ : 3-*dimethoxychalkone*,

$$OMe\cdot C_6H_3(OH)\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)\cdot OH,$$

which crystallises from alcohol in yellow needles, m. p. 142—143°. The *diacetyl* derivative, $C_{21}H_{20}O_7$, forms yellow prisms, m. p. 155°. 2′ : 4-*Dihydroxy*-5′ : 3-*dimethoxychalkone*, $C_{17}H_{16}O_5$, prepared from vanillin and quinacetophenone monomethyl ether, crystallises from alcohol in orange-coloured plates, m. p. 122—123°. 4-*Hydroxy*-3-*methoxystyryl* 1-*hydroxynaphthyl* 2-*ketone*,

$$OH\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO\cdot C_{10}H_6\cdot OH,$$

prepared from vanillin, 2-aceto-1-naphthol, alcohol, and sodium hydroxide solution, crystallises from alcohol in red needles, m. p. 190—191°. Its solution in concentrated sulphuric acid has a reddish-yellow colour. The *diacetyl* derivative, $C_{24}H_{20}O_6$, crystallises in yellow needles, m. p. 162—164°.

The presence of the CO·C:C group in curcumin is proved by the fact that ferulic acid (4-hydroxy-3-methoxycinnamic acid) is formed when curcumin is boiled with 20% potassium hydroxide solution. The formula $[OH\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO]_2CH_2$ is suggested as accounting for all the properties of curcumin. The formula $C_{21}H_{20}O_6$ (compare Latham and Loring Jackson, Abstr., 1908, i, 670) has been confirmed by conversion of curcumin into its *dicarbomethoxy*-derivative,

$$C_{19}H_{12}O_2(O\cdot CO_2Me)_2(OMe)_2,$$

deep yellow prisms, m. p. 150°, and its *dicarboethoxy*-derivative,

$$C_{19}H_{12}O_2(O\cdot CO_2Et)_2(OMe_4)_2,$$

yellow plates, m. p. 149—150°.

Hydroxylamine reacts with the dicarbethoxy-derivative, yielding 3 : 3′-*dimethoxy*-4 : 4′-*dicarbethoxy*-αγ-*distyryl*-*isooxazole*,

$$CH{<}\begin{matrix}C[CH:CH\cdot C_6H_3(OMe)(OH)]:N\\ C[CH:CH\cdot C_6H_3(OMe)(OH)]\cdot O\end{matrix}$$

as colourless plates, m. p. 139—140°. The same compound can also be obtained by the action of ethyl chloroformate on Ciamician and Silber's oxime-anhydride, $C_{21}H_{19}O_5N$ (Abstr., 1897, i, 229).

J. J. S.

C- and O-Acyl Derivatives of Coumaranones or 2-Hydroxycoumarones. KARL AUWERS (*Ber.*, 1910, 43, 2192—2202).—By the interaction of organic bases and esters of 3-chloroacetyl-*p*-cresol, compounds of the type $C_6H_3Me(OH)\cdot CO\cdot CH_2\cdot NPh\cdot COR$ are formed, together with other substances containing nitrogen (compare Auwers, Abstr., 1909, i, 222). In presence of weak alkalis, the reaction takes quite another course, nitrogen-free substances being the sole product. These were at first taken to be flavonols or chromonols, but this idea was disproved by comparison with 2-methylflavonol, and the new compounds shown to be keto-derivatives of 4-methylcoumarone,

$$C_6H_3Me{<}\begin{matrix}C(OH)\\ O\end{matrix}{>}C\cdot COR.$$

They form salts, ethers, and esters, and where $R = CH_3$ behave as ketones, although when R is an aromatic radicle, steric influences

prevent the formation of ketonic derivatives. Of the three possible desmotropic structural formulæ for the new compounds, the above is shown to be the most probable, and they are 1- or *C*-acyl-2-hydroxy-coumarone derivatives, isomeric with the *O*-acyl compounds,

$$C_6H_4<\begin{matrix}C\cdot O\cdot COR\\O\end{matrix}>CH,$$

formed by acylation of coumaranones. The esters of the new ketones represent mixed *O,C*-diacyl derivatives. 3-Chloroacetyl-*p*-cresol forms an *anisoyl* derivative crystallising in short, lustrous, pointed prisms, m. p. 121·5°.

2-*Hydroxy*-1-*benzoyl*-4-*methylcoumarone*,

$$C_6H_3Me<\begin{matrix}C(OH)\\O\end{matrix}>C\cdot CO\cdot C_6H_5,$$

produced by boiling a mixture of 3-chloroacetyl-*p*-cresol, potassium carbonate and benzene, has m. p. 112°, and crystallises from alcohol in pale yellow, silky needles, which change readily into short, lustrous, four-sided plates. The compound forms a sparingly soluble *sodium* salt, dissolves in sodium hydroxide with an intense yellow coloration, and in sulphuric acid gives a yellow solution with a green fluorescence. It does not react with ketone reagents. The *acetate* crystallises in stellar aggregates of short, glistening needles, m. p. 81—82°. The *benzoate* forms colourless, glistening prisms, m. p. 137°.

2-*Hydroxy*-1-*anisoyl*-4-*methylcoumarone* forms long, slender, sulphur-yellow, lustrous needles, m. p. 145·5°.

2-*Hydroxy*-1-*acetyl*-4-*methylcoumarone*, $C_6H_3Me<\begin{matrix}C(OH)\\O\end{matrix}>C\cdot COMe$, crystallises in long, glistening needles, m. p. 86—87°; it is coloured orange-yellow by sulphuric acid. Alkaline hydrogen peroxide oxidises it to *p*-homosalicylic acid. The *benzoate* separates in colourless, matted needles, m. p. 128—129°; the *semicarbazone* forms colourless or slightly yellow needles, which become yellow at 195°, m. p. 202° (decomp.). The *phenylhydrazone* forms long, yellow needles, m. p. 128°.

2-*Benzoyloxy*-4-*methylcoumarone*, $C_6H_3Me<\begin{matrix}C(OBz)\\O\end{matrix}>CH$, prepared from methylcoumaranone, benzoyl chloride, and sodium hydroxide, forms yellow needles, m. p. 64—65°. E. F. A.

The Coumarone Group. A. von Graffenried and Stanislaus von Kostanecki (*Ber.*, 1910, 43, 2155—2157. Compare Abstr., 1908, i, 442; 1909, i, 319).—Ethyl bromoacetate reacts with quinaceto-phenone monomethyl ether in the presence of sodium ethoxide, yielding *ethyl* 2-*acetyl*-4-*methoxyphenoxyacetate*, $OMe\cdot C_6H_3Ac\cdot O\cdot CH_2\cdot CO_2Et$, and this when hydrolysed with alcoholic potassium hydroxide yields the corresponding *acid*, $C_{11}H_{12}O_5$, which crystallises in broad needles, m. p. 144—145°. 4-*Methoxy*-2-*methylcoumarone*,

$$OMe\cdot C_6H_3<\begin{matrix}O\\CMe\end{matrix}>CH,$$

obtained by heating the acid with acetic anhydride and sodium acetate, is a colourless oil, b. p. 245°/706 mm., with an aromatic odour. Its

solution in concentrated sulphuric acid has an orange colour with a green fluorescence.

2-*Acetyl-4-ethoxyphenoxyacetic acid*, $OEt \cdot C_6H_3Ac \cdot O \cdot CH_2 \cdot CO_2H$, crystallises in needles, m. p. 138—139°, and 4-*ethoxy-2-methylcoumarone*, $C_{11}H_{12}O_2$, is a colourless oil, b. p. 257°/718 mm.

2-*Acetyl*-5 : 6-*dimethoxyphenoxyacetic acid*,

$$C_6H_2Ac(OMe)_2 \cdot O \cdot CH_2 \cdot CO_2H,$$

obtained from gallacetophenone methyl ether, has m. p. 104—106°, and 5 : 6-*dimethoxy-2-methylcoumarone*, $C_6H_2(OMe)_2{<}{\substack{O\text{--}\\ CMe}}{>}CH$, has b. p. 278—279°/702 mm. J. J. S.

Derivatives of 2-Styrylcoumarone. J. Abelin and Stanislaus von Kostanecki (*Ber.*, 1910, **43**, 2157—2162. Compare preceding abstract).—2-*Cinnamoyl-5-methoxyphenoxyacetic acid*,

$$CHPh\colon CH \cdot CO \cdot C_6H_3(OMe) \cdot O \cdot CH_2 \cdot CO_2H,$$

obtained by condensing benzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid (Abstr., 1909, i, 319) in the presence of alkali, crystallises from alcohol in colourless plates, m. p. 166—167°. The *ethyl* ester, $C_{20}H_{20}O_5$, forms colourless needles, m. p. 89°. 5-*Methoxy-2-styrylcoumarone*, $OMe \cdot C_6H_3{<}{\substack{O \cdot CH \\ \| \\ C \cdot CH\colon CHPh}}$, is formed when the acid is heated with acetic anhydride and sodium acetate. It crystallises from alcohol in colourless needles, m. p. 77—78°, and gives a bright red colour when moistened with concentrated sulphuric acid.

5 : 2′-*Dimethoxy-2-cinnamoylphenoxyacetic acid*,

$$OMe \cdot C_6H_4 \cdot CH\colon CH \cdot CO \cdot C_6H_3(OMe) \cdot O \cdot CH_2 \cdot CO_2H,$$

obtained from *o*-methoxybenzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid, crystallises from alcohol in yellow prisms or colourless needles, m. p. 128°. The *ethyl* ester, $C_{21}H_{22}O_6$, has m. p. 111°, and 5 : 2′-*dimethoxy-2-styrylcoumarone*, $C_{18}H_{16}O_3$, crystallises from alcohol in rhombic p'ates, m. p. 75°.

5 : 3′-*Dimethoxy-2-cinnamoylphenoxyacetic acid*, $C_{19}H_{18}O_6$, forms colourless needles, m. p. 142—143°; its *ethyl* ester, $C_{21}H_{22}O_6$, has m. p. 96°, and 5 : 3′-*dimethoxy-2-styrylcoumarone*, $C_{18}H_{16}O_3$, crystallises in needles or plates, m. p. 120—121°.

5 : 4′-*Dimethoxy-2-cinnamoylphenoxyacetic acid* has m. p. 162—163°; its *ethyl* ester has m. p. 117°, and 5 : 4′-*dimethoxy-2-styrylcoumarone* has m. p. 126°.

5 : 3′ : 4′-*Trimethoxy-2-cinnamoylphenoxyacetic acid*,

$$C_6H_3(OMe)_2 \cdot CH\colon CH \cdot CO \cdot C_6H_3(OMe) \cdot O \cdot CH_2 \cdot CO_2H,$$

obtained from veratraldehyde, crystallises in plates, m. p. 175°, and gives a dark red coloration with concentrated sulphuric acid. The *ethyl* ester, $C_{22}H_{24}O_7$, crystallises in yellow plates, m. p. 129—130°, and 5 : 3′ : 4′-*trimethoxy-2-styrylcoumarone*, $C_{19}H_{18}O_4$, forms colourless needles, m. p. 106°. Its solution in sulphuric acid has a magenta-red colour. All attempts to transform this compound into a trimethoxydihydro*iso*brasan by ring formation proved fruitless. J. J. S.

Formation of Pyrene from Thebaine. Martin Freund (*Ber.* 1910, **43**, 2128—2130).—The formation of pyrene from thebaine is

confirmed (compare Freund, Abstr., 1897, i, 496). Pyrene is formed, not merely when the alkaloid is distilled with zinc dust, but also when it is reduced with hydriodic acid and red phosphorus. The latter fact invalidates to a large extent Pschorr's criticism (this vol., i, 423) of the author's formula for thebaine. J. J. S.

New Preparation of 1-Alkylpyrrolidines. KARL LÖFFLER (*Ber.*, 1910, **43**, 2035—2048. Compare Abstr., 1909, i, 830).—The method previously described, bromination of an amine at the nitrogen atom and elimination of hydrogen bromide by means of concentrated sulphuric acid, has been extended to the preparation of 1-methyl-2-propylpyrrolidine and of 1 : 2-dimethyl-, 1-methyl-2-ethyl-, and 1 : 3-dimethyl-pyrrolidines. Attempts were made to extend it to such amines as would yield piperidine derivatives or four-membered rings, but without result.

[With CURT FREYTAG.]—*δ-Methylamino*-n-*heptane*, prepared from methylamine and dipropyl ketone, and subsequent reduction, has b. p. 148°, D^{15} 0·77; the *aurichloride* separates in well formed yellow needles, m. p. 99°; the *platinichloride* forms orange plates, m. p. 193—195°; the *picrate* separates in long, light yellow needles, m. p. 96°; the *hydrochloride* is very hygroscopic.

1-*Methyl*-2-*propylpyrrolidine* is a colourless liquid, b. p. 146—147°/761 mm., D^{15} 0·815. The *picrate* forms yellow needles, m. p. 124°; the *platinichloride* forms orange plates, m. p. 145—146°; the *aurichloride* also forms yellow plates, m. p. 76°. The *ethochloride* gives a *platinichloride*, orange plates, m. p. 226—227°, and an easily decomposed yellow *aurichloride*.

Methyl-n-*amylamine* has b. p. 116—118°, D_4^{15} 0·738; the *picrate* forms yellow needles, m. p. 119—120°; the *hydrochloride* forms needles, m. p. 181—182°; the *platinichloride* separates in yellow needles, m. p. 171—173°; the *aurichloride* is a yellow oil. It could be converted into 1-methylpiperidine in the manner described.

β-Methylamino-n-*butane* has b. p. 78—79°, D^{15} 0·74; the *aurichloride* forms yellow needles, m. p. 58°; the *platinichloride* forms dark orange crystals, m. p. 151°; the *picrate* forms light yellow needles, m. p. 78°. No ring compound was formed on heating the brominated amine with concentrated sulphuric acid.

[With MARIAN LUKOWSKY.]—Methyl*iso*amylamine (compare Stoermer and Lepel, Abstr., 1896, i, 663) has b. p. 108—110°, D_4^{22} 0·7428; hydrochloride, m. p. 181°; platinichloride, m. p. 208—209°; aurichloride, needles, m. p. 68—70°; *picrate*, m. p. 112°.

1 : 3-*Dimethylpyrrolidine* has an odour of piperidine, b. p. 96—97°, D_4^{15} 0·792. The *picrate* shows dimorphism, separating first in long crystals, m. p. 181—182°, which change when kept in alcoholic solution into granular crystals, m. p. 110—115°: these on recrystallisation give the less fusible variety. The *hydrochloride* is hygroscopic; the *platinichloride* forms garnet-red, granular crystals, m. p. 58—59°; the *aurichloride* crystallises in characteristic, feathery, interlaced needles, m. p. 137°; the *mercurichloride* has m. p. 200—201°. The *ethiodide* is a hygroscopic, colourless powder; of the *ethochloride* the

platinichloride has m. p. 243—244° (decomp.); the *aurichloride*, m. p 200—201°.

[With WALDEMAR BOBILOFF.]—*β-Methylamino*-n-*pentane*, from methylamine and methyl propyl ketone, is a colourless, mobile liquid, b. p. 103—104°/754 mm., D^{20} 0·747. The *platinichloride* forms yellowish-red needles, m. p. 137·5°; the *aurichloride* is an oil; the *picrate* forms broad needles, m. p. 77—78°. It is readily converted into 1 : 2-dimethylpyrrolidine, of which the *picrate* has m. p. 233·5°, and the *platinichloride* of the *ethochloride*, m. p. 249° (decomp.).

γ-Methylaminohexane is a transparent, mobile, strongly basic liquid, b. p. 126—128°/754 mm., D^{20} 0·761. The *platinichloride* is a flesh-coloured powder, m. p. 162—163°; aurichloride and picrate are oily.

1-*Methyl*-2-*ethylpyrrolidine* is a transparent, strongly basic liquid, b. p. 122—123°/762 mm., D^{15} 0·8124. The *platinichloride* forms intergrown needles, m. p. 210—211°; the *aurichloride*, well formed needles, m. p. 112°; the *picrate*, golden-yellow plates, m. p. 170°. The *platinichloride* of the *ethochloride* begins to decompose at 243°, m. p. about 250°. E. F. A.

Synthesis of δ-Methylconidine and of Derivatives of 2-Methyl-6-ethylolpiperidine. KARL LÖFFLER and HANS REMMLER (*Ber.*, 1910, **43**, 2048—2059. Compare Königs and Happe, Abstr., 1903, i, 850; Löffler and Thiel, Abstr., 1909, i, 182).—By the condensation of 2 : 6-lutidine with formaldehyde, 2-methyl-6-ethylolpyridine, b. p. 126—128°/16 mm., and 2 : 6-diethylolpyridine, b. p. 185—195°/16 mm., are obtained. The former, when reduced by means of sodium and alcohol, gives 2-*methyl*-6-*ethylolpiperidine*; the crude base has b. p. 226—232°, and is a mixture of stereoisomerides. One form separates from ether in glistening, rhombic crystals, m. p. 95—96°; the *aurichloride* has m. p. 104°; the *platinichloride* forms broad crystals, m. p. 180—181°; the *picrate* has m. p. 127°. The stereoisomeride was obtained as a viscid syrup, of which the *picrate* separates in long needles, m. p. 187°; the *aurichloride* has m. p. 99—100°; the *platinichloride* forms short, granular crystals, m. p. 198—199°.

2-Methyl-6-ethylolpiperidine has very little poisonous action. Attempts to resolve it into optically active modifications by means of tartaric acid were not successful.

When heated under pressure with fuming hydrochloric acid and red phosphorus, a *hydriodide iodide* is formed, crystallising in colourless, short needles, m. p. 192—193°. On warming with sodium hydroxide, this is converted into δ-*methylconidine*, $\begin{array}{l} CH_2\cdot CH_2—CH\cdot CH_2 \\ | \qquad\qquad\quad | \qquad | \\ CH_2\cdot CHMe\cdot N—CH_2 \end{array}$, a colourless, mobile liquid with an unpleasant coniceine-like odour, b. p. 156°, D_4^{15} 0 8931. The *picrate* forms large, pointed needles, m. p. 237°; the *aurichloride* is amorphous, m. p. 191—192°; the *platinichloride* forms broad needles, m. p. 198°. The *ethiodide* has m. p. 202° (decomp.); the *platinichloride* of the *ethochloride* has m. p. 210·5°.

By the action of phosphorus pentachloride on 2-methyl-6-ethylolpiperidine, 2-*methyl*-6-*vinylpiperidine* is obtained; the colourless, mobile liquid has b. p. 150°, D_4^{15} 0·8381. The *hydrochloride* forms colourless, slender needles, m. p. 242·5—243°; after crystallisation of

the salt, the mother liquors become an intense red colour after a time. The *picrate* crystallises in tabular plates, m. p. 123°; the *platinichloride* in long needles, m. p. 176°.

Chromic acid oxidises 2-methyl-6-ethylolpiperidine to *2-methylpiperidyl-6-acetic acid*, crystallising in colourless, matted needles, m. p. 219—220°. The *hydrochloride* crystallises similarly, m. p. 192—206° (decomp.); the *aurichloride* forms needles, m. p. 129—131°; the *platinichloride*, granular crystals, m. p. 207°.

2 : 6-*Diethylolpiperidine* is obtained by reducing diethylolpyridine as a viscid oil, b. p. 168—169°/18 mm.; it crystallises in reniform aggregates. The *picrate* has m. p. 136°.

On acetylating 2-methyl-6-ethylolpiperidine with warm acetic anhydride, a *diacetate* is formed, a colourless, viscid liquid, b. p. 190—200°/25 mm., D_4^{15} 1·703; the two acetyl groups are probably attached to nitrogen and in the side-chain respectively; both are hydrolysed by 1% alcoholic hydrochloric acid. Acetylation in the cold with acetic anhydride gives the *monoacetate*, b. p. 105—110°/25 mm., a mobile, colourless, strongly alkaline liquid, which forms stable salts, and therefore is acetylated in the side-chain. The *aurichloride* crystallises in reniform aggregates, m. p. 118°. It was not found possible to cause this acetyl group to wander to the nitrogen atom. E. F. A.

Stereochemistry of Quinquevalent Nitrogen. MAX SCHOLTZ (*Ber.*, 1910, **43**, 2121—2126. Compare Abstr., 1904, i, 1044; 1905, i, 296, 473; 1908, i, 678; Scholtz and Wassermann, 1907, i, 340; Voss and Gadamer, this vol., i, 415).—Two stereoisomeric quaternary ammonium salts are formed by the union of allyl iodide with *dl*-6-phenyl-2-methyl-1-ethylpiperidine, and from these quaternary salts well defined, crystalline isomeric platinichlorides have been prepared.

Stereoisomeric quinquevalent nitrogen compounds of the type Na_2bcd have been prepared by condensing *o*-xylylene bromide with 2-phenyl-6-methylpiperidine (compare Abstr., 1898, i, 565). These compounds differ from the stereoisomerides described by Aschan (Abstr., 1904, i, 350), as they contain only one nitrogen atom.

6-*Phenyl-2-methyl-1-propylpiperidine*, $NPr<{CHMe-CH_2 \atop CHPh-CH_2}>CH_2$, prepared by boiling 2-phenyl-6-methylpiperidine (Scholtz and Müller, Abstr., 1901, i, 41) with *n*-propyl iodide and potassium hydroxide, is a colourless liquid with a basic odour, has b. p. 264—265° (corr.) and D_4^{20} 0·9101. It combines with benzyl iodide, yielding an oily *2-phenylbenzyl-6-methyl-n-propylpiperidinium iodide*, $C_{22}H_{30}NI$, from which only a small amount of colourless crystals were isolated.

dl-2-*Phenyl-6-methyl-1-ethyl-1-allylpiperidinium iodide*,

$$C_3H_5\cdot NEtI<{CHMe\cdot CH_2 \atop CHPh-CH_2}>CH_2,$$

exists in an oily (α) and a crystalline (β) form. The latter forms colourless prisms, m. p. 198°. The α-*platinichloride*, $(C_{17}H_{26}N)_2PtCl_6$, crystallises in orange-red needles, m. p. 211° (decomp.); the isomeric compound forms similar needles, m. p. 223°. The two *hydrochlorides* are deliquescent solids. The α-*aurichloride* is an oil which solidifies to

a resinous mass, and the *β-aurichloride*, $C_{17}H_{26}NAuCl_4$, crystallises in golden, yellow needles, m. p. 136°.

a-2-Phenyl-1-o-xylylene-6-methylpiperidinium bromide,

$$C_6H_4{<}{CH_2 \atop CH_2}{>}NBr{<}{CMe\text{-}CH_2 \atop CPh\text{-}CH_2}{>}CH_2,$$

crystallises from water in rhombic prisms, m. p. 226°. The *β-compound* separates from solvents as an oil which solidifies when rubbed; it has m. p. 228°. The *a-platinichloride* has m. p. 238°, and the β-compound, m. p. 259°. The aurichlorides are oily. J. J. S.

An Acetato-Pyridine-Iron Base and a Very Basic Pyridine-containing Ferric Acetate. RUDOLF WEINLAND and E. GUSSMANN (*Ber.*, 1910, **43**, 2144—2149).—By the action of pyridine on the acetate of the hexa-acetato-triferri-base (Abstr., 1909, i, 872), brownish-yellow salts have been obtained containing two atoms of iron and two molecules of pyridine in the cation.

$$\left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop OH}}\right](OAc)_2$$

The *acetate* (annexed formula) is obtained by leaving 20 grams of the monoacetate of the hexa-acetato-triferri-base in contact with 50—60 grams of anhydrous pyridine at the ordinary temperature. The monoacetate dissolves, and then the acetate of the acetato-pyridine-iron base separates as a brownish-yellow powder, consisting of microscopic four-and six-sided plates.

$$\left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop OH}}\right]{OAc \atop I}$$

The *iodide* (annexed formula) separates as a brownish-yellow precipitate when a saturated solution of potassium iodide is added to the freshly prepared solution of the acetate. The *thiocyanate*,

$$\left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop OH}}\right](CNS)_2 + \left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop OH}}\right]{OAc \atop CNS},$$

separates as a chocolate-brown powder on the addition of a saturated solution of sodium thiocyanate to the aqueous solution of the acetate. Under the same conditions, a saturated solution of potassium permanganate gives a rose-red precipitate of the permanganate,

$$\left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop (OH)_2}}\right]MnO_4 + \left[Fe_2{(OAc)_3 \atop {(C_5H_5N)_2 \atop OH}}\right](OAc)_2.$$

When 5 grams of pyridine are added to 30 c.c. of a 12% solution of the monoacetate of the hexa-acetato-triferri-base (*loc. cit.*) and the solution maintained at a temperature not exceeding 15°, dark red crystals of a pyridine-containing basic ferric acetate,

$$Fe_2O(OH)(OAc)_3{\cdot}C_5H_5N,$$

separate after some hours. A copper-red acetate of a pyridine-containing acetato-iron base has also been obtained, but requires further investigation. T. S. P.

Derivatives of Tetrahydroquinoline. III. Ketones and Acids of Tetrahydroquinoline and of Tetrahydro-*o*- and *p*-toluquinoline. FRANZ KUNCKELL (*Ber. Deut. pharm. Ges.*, 1910, **20**, 277—293).—The interaction of 1-acetyltetrahydroquinoline, chloroacetyl chloride, and aluminium chloride in carbon disulphide leads to

the formation of 1-*acetyl*-6-*chloroacetyltetrahydroquinoline*,

$$CH_2Cl\cdot CO\cdot C_6H_3<\begin{matrix}CH_2-CH_2\\ NAc\cdot CH_2\end{matrix},$$

m. p. 137°, which is converted into 1-*acetyltetrahydroquinoline*-6-*carboxylic acid*, m. p. 187°, by hot alkaline hydrogen peroxide, into a *trinitrotetrahydroquinoline*, m. p. 152°, by concentrated nitric acid, and into 1-*acetyl*-6-*chlorobromoacetyltetrahydroquinoline*, m. p. 179°, by bromination in glacial acetic acid; the last-mentioned compound is oxidised to the preceding acid, m. p. 187°, by alkaline hydrogen peroxide. The hydrolysis of 1-acetyl-6-chloroacetyltetrahydroquinoline by 20% hydrochloric acid on the water-bath yields 6-*chloroacetyltetrahydroquinoline*, m. p. 123—124°, an alcoholic solution of which at 5—10° is converted by nitrous fumes into the *nitrosoamine*, m. p. 140°.

1-*Acetyl*-6-*bromoacetyltetrahydroquinoline* has m. p. 134°.

1-Acetyl-6-methyltetrahydroquinoline is not only attacked more readily than 1-acetyltetrahydroquinoline by chloroacetyl chloride or bromoacetyl bromide, but reacts even with acetyl bromide itself, which is not the case with 1-acetyltetrahydroquinoline. 1-?-*Diacetyl*-6-*methyltetrahydroquinoline* has m. p. 160°. 1-*Acetyl*-?-*chloroacetyl*-6-*methyltetrahydroquinoline*, m. p. 132°, and 1-*acetyl*-?-*bromoacetyl*-6-*methyltetrahydroquinoline*, m. p. 128°, are obtained in the same manner as 1-acetyl-6-chloroacetyltetrahydroquinoline, and are converted into the following substances by reactions similiar to those mentioned above: 1-*acetyl*-6-*methyltetrahydroquinolinecarboxylic acid*,

$CO_2H\cdot C_6H_2Me<\begin{matrix}CH_2-CH_2\\ NAc\cdot CH_2\end{matrix}$, m. p. 201°; *chloroacetyl*-6-*methyltetrahydroquinoline*, m. p. 122°, (*hydrochloride*, m. p. 218°); 1-*acetyl*-?-*chlorobromoacetyl*-6-*methyltetrahydroquinoline*, m. p. 143°; when heated with concentrated nitric acid, 1-acetyl-?-chloroacetyl-6-methyltetrahydroquinoline yields a *substance*, m. p. 259° (decomp.), which is probably a nitropiperidinecarboxylic acid.

The following derivatives of 1-acetyl-8-methyltetrahydroquinoline are obtained by similar processes: 1-*acetyl*-?-*chloroacetyl*-8-*methyltetrahydroquinoline*, m. p. 120°; 1-*acetyl*-?-*bromoacetyl*-8-*methyltetrahydroquinoline*, m. p. 125—126°; 1-*acetyl*-8-*methyltetrahydroquinolinecarboxylic acid*, m. p. 108°; the acetyl group cannot be introduced into 1-acetyl-8-methyltetrahydroquinoline. C. S.

Method of Preparation of α-Benzoylated Phenylhydrazines. Georg Lockemann (*Ber.*, 1910, **43**, 2223—2230).—Lockemann and Liesche (Abstr., 1905, i, 570) have shown that by the action of benzoyl chloride on phenylethylidenehydrazine in presence of dry pyridine, α-benzoyl-α-phenyl-β-ethylidenehydrazine is obtained. It is absolutely necessary to exclude all traces of moisture, otherwise the ethylidene group is eliminated, and di- and tri-benzoyl derivatives are obtained. Using dry pyridine, it is possible to benzoylate also with *m*- and *p*-nitro- and *p*-chloro-benzoyl chloride, but not with the *o*-nitro-derivative.

The action of excess of mineral acids in cold solution eliminates the ethylidene group from these hydrazines as aldehyde, and the salts of α-benzoylhydrazones are obtained.

[With TH. LOBENSTEIN, H. ENDE, and F. HEROLD.]—α-Benzoyl-α-phenyl-β-ethylidenehydrazine forms colourless, rectangular plates, m. p. 90—91°. It gives α-benzoylphenylhydrazine (Michaelis and Schmidt, Abstr., 1887, 820), m. p. 70°; the hydrochloride forms colourless needles, m. p. 202°.

α-p-*Nitrobenzoyl-α-phenyl-β-ethylidenehydrazine* crystallises in light yellow prisms with pointed ends, m. p. 116—117°; alcoholic hydrogen chloride converts it into the *hydrochloride* of α-p-*nitrobenzoyl-α-phenylhydrazine*, also crystallising in light yellow needles, which sinter at 183°, m. p. 195—196° (decomp.). The free base forms light yellow, lustrous crystals, m. p. 141—142°; the acetyl derivative, α-p-*nitrobenzoyl-β-acetyl-α-phenylhydrazine*, separates in light yellow crystals, m. p. 184—185°.

α-m-*Nitrobenzoyl-α-phenyl-β-ethylidenehydrazine* forms yellowish-white plates, m. p. 124—125°; α-m-*nitrobenzoylphenylhydrazine* forms yellowish-white, six-edged plates, m. p. 123—124°; the *hydrochloride* crystallises in yellowish-white, pointed needles, m. p. 176—177° (decomp.).

α-p-*Chlorobenzoyl-α-phenyl-β-ethylidenehydrazine* was obtained in yellow, short, rhombic crystals and in colourless, reniform prisms, both m. p. 90—91°. On keeping, the colourless prisms slowly change to the yellow, stable form; on crystallisation, the labile, colourless forms are the first to separate.

When moisture is present, p-*chlorobenzoic anhydride* is obtained, instead of the foregoing; it crystallises in lustrous, long, colourless prisms and needles, m. p. 193—194°.

α-p-*Chlorobenzoyl-α-phenylhydrazine* forms colourless rhombs with pointed angles, m. p. 128—129°. The *hydrochloride* crystallises in colourless, lustrous needles, m. p. 192—193°. E. F. A.

Syntheses of Polypeptides. Derivatives of Pyrrolidonecarboxylic Acid. EMIL ABDERHALDEN and AKIKAZU SUWA (*Ber.*, 1910, **43**, 2151—2155).—*Pyrrolidonecarboxylic chloride* can be obtained by the action of thionyl chloride or of a mixture of acetyl chloride and phosphorus pentachloride on the acid, and condenses with ethyl glycine, yielding *ethyl pyrrolidonylglycine*, $C_9H_{14}O_4N_2$, which crystallises from alcohol in colourless needles, m. p. 134° (corr.). When hydrolysed with concentrated hydrochloric acid, the ester yields the hydrochlorides of glutamic acid and of glycine ester.

Pyrrolidonylglycine, $\begin{matrix}CH_2\cdot CH_2\\ | \qquad\quad \\ CO—NH\end{matrix}\!\!>CH\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, can be prepared by hydrolysing the ester by shaking with *N*-sodium hydroxide solution; it crystallises in slender needles, m. p. 168° (corr.), and yields a hygroscopic *copper* salt, $(C_7H_9O_4N_2)_2Cu,2H_2O$. J. J. S.

Quinone Di-imines of the Acridone Series. LUDWIG KALB (*Ber.*, 1910, **43**, 2209—2214).—By the oxidation of the yellow quinacridone discovered by Ullmann and Maag (Abstr., 1906, i, 459) with lead oxide in indifferent solvents in presence of acetic acid, a new quinonedi-imine, *dehydroquinacridone*,

$$C_6H_4{<}{}^{CO}_{N}{>}C_6H_2{<}{}^{N}_{CO}{>}C_6H_4,$$

is obtained, which has a remarkable greenish dark-blue colour in solution.

It may be regarded as derived from quinonedianil,

$$C_6H_5\cdot N:C_6H_4:N\cdot C_6H_5,$$

which is orange-red; the colour is deepened to blue by the presence of the two acridone rings. The corresponding compound with but one acridone ring, *dehydro-2-anilinoacridone*, $C_6H_4<\substack{CO \\ N}>C_6H_3:N\cdot C_6H_5$, obtained by the oxidation of 2-anilinoacridone with lead oxide, is dark red.

Dehydroquinacridone, like dehydroindigotin, has a strong oxidising action, and liberates other quinones and quinonedi-imines from their hydro-compounds, and oxidises indigotin to dehydroindigotin. The oxidising power may be determined by titration with ethereal quinol solution, the colour changing from blue through green to yellow. It liberates chlorine from cold fuming hydrochloric acid.

2-Anilinodehydroacridone does not possess such marked oxidising powers, but oxidises quinol to quinone.

Dehydroquinacridone crystallises in bluish-black, hexagonal plates. It dissolves in sulphuric acid with decomposition, showing a brownish-yellow coloration and green fluorescence.

4'-Anilinodiphenylamine-2-carboxylic acid,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NHPh,$$

prepared by the condensation of *p*-aminodiphenylamine with *o*-chlorobenzoic acid, crystallises in pale yellow plates, m. p. 199° (green coloration and decomp.). The colourless solution in sulphuric acid gives a cherry-red coloration with traces of nitric acid.

2-Anilinoacridone, prepared by warming the above compound with sulphuric acid at 85°, forms yellow, crystalline crusts, m. p. 303—305°. The solutions are yellow and fluoresce green; that in sulphuric acid is faintly red, and has an intense blue fluorescence. The *hydrochloride* forms long, red, prismatic plates, which change to yellow at 250°.

2-Anilinodehydroacridone forms long, pointed, blackish-brown plates, which partly melt at 145°, decomp. 280°. It dissolves and decomposes in sulphuric acid with a reddish-brown colour and blue fluorescence.

E. F. A.

Derivatives of Iminazole [Glyoxaline] and Histidine containing Iodine. HERMANN PAULY (*Ber.*, 1910, 43, 2243—2261. Compare Pauly and Gundermann, Abstr., 1909, i, 71).—It has been shown for tri-iodoglyoxaline that all three carbon atoms in the ring can fix iodine, and the preparation of a hydrochloride showed that no iodine was attached to nitrogen. This constitution is now confirmed by the preparation of a *silver* compound and of an N-*ethyl* derivative, and, further, by the continued action of iodine and alkali, leading to the formation of 1 : 2 : 4 : 5-*tetraiodoglyoxaline*, $\begin{array}{l}CI\cdot NI \\ \| \\ CI-N\end{array}\!\!>CI$. In addition, 4 : 5-*di-iodo-2-methylglyoxaline*, from 2-methylglyoxaline, 1 : 4 : 5-*tri-iodo-2-methylglyoxaline*, and 1-*iodo*-2 : 4 : 5-*trimethylglyoxaline*, $\begin{array}{l}CMe\cdot NI \\ \| \\ CMe-N\end{array}\!\!>CMe$, have

been prepared so as to allow of a comparison between glyoxalines containing iodine attached to C or N.

The C-compounds are more soluble, more definitely crystalline, they form metallic and acid salts, and melt without much loss of iodine.

The N-compounds are sparingly soluble in indifferent solvents, form a fine powder without crystalline structure, give no salts, and explode on heating, giving iodine vapour and leaving a black residue.

2:4:5-Tri-iodo-1-ethylglyoxaline, when boiled with sodium hydroxide, develops a strong odour of ethylcarbylamine.

Tetraiodoglyoxaline when heated decomposes at 160° into iodine and a black residue, which contains all the nitrogen, and about 25% of the iodine of the original substances. This iodine is not removed until the residue is heated to 400°, when it has the composition C_3N_2. At a temperature near a red heat, above 500°, this in turn decomposes to carbon and nitrogen. This behaviour is similar to that of cyanuric iodide, $C_3N_3I_3$, studied by Klason (Abstr., 1886, 1001).

Three derivatives of histidine, namely, benzoyl- and *p*-nitrobenzoylhistidine and *l*-histidine anhydride, have been iodised; in each case two iodine atoms become attached to carbon in the glyoxaline nucleus, and the compounds are regarded as derivatives of the unknown di-iodohistidine, $CI \lessgtr \begin{matrix} N - CI \\ \quad \| \\ NH \cdot C \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H \end{matrix}$.

Preparation of the *disilver* salt in the case of *tetraiodohistidine anhydride* proved the nitrogen groups to have no iodine attached to them.

Iodine is the more easily introduced into glyoxalines the more basic they are; thus, 5-methylglyoxaline decolorises nearly 7/10 mol. iodine, glyoxaline only about 1/7 mol. Histidine and histidine anhydride behave much as glyoxaline, but the introduction of acyl residues, causing the bases to react acid towards litmus, almost destroys the power of taking up iodine.

The amount of iodine absorbed by sturine corresponds almost exactly with that required by the histidine contained in sturine.

Tri-iodoglyoxaline in small doses causes a marked quickening of the breathing and of the pulse.

2 : 4 : 5-*Tri-iodo-1-ethylglyoxaline* forms colourless crystals, m. p. 141—142°.

1 : 2 : 4 : 5-*Tetraiodoglyoxaline* is a colourless or yellowish-grey, odourless powder, decomp. 160°.

4 : 5-*Di-iodo-2-methylglyoxaline* crystallises in centimetre-long, thin, lustrous prisms, m. p. 199°; it dissolves in acids or alkalis, forming salts.

1 : 4 : 5-*Tri-iodo-2-methylglyoxaline* is a greyish-yellow, insoluble powder, decomp. 160°.

1-*Iodo-2 : 4 : 5-trimethylglyoxaline* is a cream-coloured, dust-like powder, m. p. 134° (decomp. and blackening).

Benzoylhistidine has m. p. 249° (Fränkel: 230°).

Benzoyldi-iodohistidine is a colourless, chalk-like powder, m. p. 161—164° in an evacuated tube.

p-Nitrobenzoyldi-iodohistidine has m. p. 172° (decomp.). Like the

foregoing, it gives an orange-red coloration with diazobenzenesulphonic acid and sodium carbonate, and forms a *silver* salt.

Tetraiodohistidine anhydride crystallises from alcohol in aggregates of minute, rectangular plates, m. p. 240° (in an evacuated tube) to a dark liquid.

The compound is amphoteric, and dissolves in both acids and alkalis; it reacts with diazobenzenesulphonic acid, dissolves in cold, strong acids without decomposition, and on heating with sulphuric acid gives iodine vapour at 150°. The *disilver* salt is at first colloidal, but subsequently flocculent; it explodes on heating.

Reduction by means of sulphites converts tetraiodohistidine anhydride into the *di-iodo*-compound; this forms a microcrystalline powder, m. p. 245° (decomp.).

Iodine is without action on alanine anhydride. E. F. A.

Carboxylic Derivatives of 3-Methyl- and 3-Phenyl-5-chloropyrazole. AUGUST MICHAELIS and OMAR SCHMIDT (*Ber.*, 1910, **43**, 2116—2120).—Only a few pyrazole compounds containing acid groups attached to N have been prepared previously (compare Thiele and Heuser, Abstr., 1896, i, 340). Such compounds can be obtained by condensing the sodium derivatives of 5-chloro-3-methyl- and 5-chloro-3-phenyl-pyrazole with the esters of halogenated fatty acids.

5-*Chloro*-3-*methylpyrazole*-1-*propionic acid*,

$$\begin{matrix}\text{CMe}{=}\text{N}\\ |\\ \text{CH}\cdot\text{CCl}\end{matrix}{>}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H},$$

prepared by heating 5-chloro-3-methylpyrazole and ethyl β-iodopropionate with alcoholic sodium ethoxide on the water-bath for several hours, forms compact crystals, m. p. 94°. When heated above its m. p., the acid yields 5-chloro-3-methylpyrazole and acrylic acid.

The *ammonium* salt crystallises with 1EtOH; the *sodium* salt, $C_6H_8N_2Cl\cdot CO_2Na$, forms small needles; the *barium* salt, $(C_6H_8N_2Cl\cdot CO_2)_2Ba,3H_2O$, crystallises in colourless plates; the *silver* salt forms a curdy precipitate; the *ethyl* ester, $C_6H_8N_2Cl\cdot CO_2Et$, forms a pale yellow oil; the *methiodide*, $C_6H_8N_2Cl\cdot CO_2H,MeI$, forms colourless prisms, m. p. 142°, and the *methiodide* of the ester has m. p. 136°.

5-*Chloro*-4-*bromo*-3-*methylpyrazole*-1-*propionic acid*,

$$\begin{matrix}\text{CMe}{=}\text{N}\\ |\\ \text{CBr}\cdot\text{CCl}\end{matrix}{>}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H},$$

obtained by brominating the previous acid in glacial acetic acid, forms compact crystals, m. p. 113°.

5-*Chloro*-3-*methylpyrazole*-1-*acetic acid* crystallises in colourless needles, m. p. 199°; the *ammonium* salt crystallises with 1EtOH; the *sodium* with $2{\cdot}5H_2O$, and the *barium* with $5H_2O$. The *ethyl* ester is a pale yellow oil; the *methiodide* has m. p. 156°, and the *methiodide* of the ethyl ester, m. p. 130°. 5-*Chloro*-4-*bromo*-3-*methylpyrazole*-1-*acetic acid*, $C_5H_5N_2ClBr\cdot CO_2H$, crystallises in nacreous plates, m. p. 197°.

Ethyl 5-*chloro*-3-*methylpyrazole*-1-*carboxylate*,

$$\text{N}{<}\begin{matrix}\text{N(CO}_2\text{Et)}\\ \text{CMe}{-}\text{CH}\end{matrix}{>}\text{CCl},$$

is a colourless oil, b. p. 127°/18 mm.; the free acid cannot be isolated, as it decomposes immediately into 5-chloro-3-methylpyrazole and carbon dioxide.

5-*Chloro*-3-*phenylpyrazole*-1-*acetic acid*, $C_{10}H_8N_2Cl{\cdot}CO_2H$, forms colourless needles, m. p. 166°. The *sodium* salt crystallises with $4{\cdot}5H_2O$, and the *barium* salt with $7H_2O$. Its 4-*bromo*-derivative, $C_{10}H_7N_2ClBr{\cdot}CO_2H$, forms colourless needles, m. p. 169°.

J. J. S.

Pyrines of 1 : 3-Dimethylpyrazolone. AUGUST MICHAELIS and AUGUST LACHWITZ (*Ber.*, 1910, **43**, 2106—2115).—5-*Chloro*-3-*methylpyrazole*, $N{<}\begin{matrix}NH{-}CCl\\ CMe{\cdot}CH\end{matrix}$, prepared by the action of phosphoryl chloride on 3-methylpyrazolone at 150°, forms needles or rhombic crystals, m. p. 116°, b. p. 258°, and when heated at 140° for six hours with phosphorus pentachloride, yields 4 : 5-*dichloro*-3-*methylpyrazole*,

$$N{<}\begin{matrix}NH{-}CCl\\ CMe{\cdot}CCl\end{matrix},$$

which crystallises in felted needles, m. p. 128°, and is insoluble in acids. 5-*Chloro*-4-*bromo*-3-*methylpyrazole*, $C_4H_4N_2ClBr$, obtained by the action of bromine on a glacial acetic acid solution of the 5-chloro-derivative, crystallises in glistening needles, m. p. 140°, and yields a *perbromide*, $C_4H_4N_2ClBr_3$, m. p. 186°. 5-*Chloro*-4-*iodo*-3-*methylpyrazolone*,

$$C_4H_4N_2ClI,$$

also forms glistening needles, m. p. 152°. 5-*Chloro*-1-*benzenesulphonyl*-3-*methylpyrazolone*, $N{<}\begin{matrix}N(SO_2Ph)\\ CMe{-}CH\end{matrix}{>}CCl$, forms colourless crystals, m. p. 67°, and with bromine yields the 4-*bromo*-derivative, m. p. 117°.

5-*Chloro*-1 : 3-*dimethylpyrazole methiodide*, $NMeI{<}\begin{matrix}NMe{\cdot}CCl\\ CMe{-}CH\end{matrix}$, prepared by heating 5-chloro-3-methylpyrazole with methyl iodide and alcohol at 100°, crystallises in colourless needles, m. p. 240°. The *methobromide* has m. p. 276°, and the *methochloride* contains $3H_2O$ and has m. p. 230°, or 252° anhydrous; the *platinichloride*,

$$(C_6H_{10}N_2Cl)_2PtCl_6,H_2O,$$

forms red, compact crystals, m. p. 243°; the *mercurichloride*,

$$C_6H_{10}N_2Cl_2,HgCl_2,$$

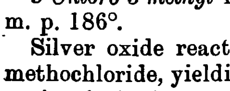
colourless plates, m. p. 136°, and the *picrate*,

$$C_6H_{10}N_2Cl,C_6H_3O_7N_3,$$

pale yellow needles, m. p. 132°.

5-*Chloro*-3-*methyl*-1-*ethylpyrazole ethiodide* forms colourless plates, m. p. 186°.

Silver oxide reacts with an aqueous solution of the methiodide, or methochloride, yielding 2 : 5-oxido-1 : 2 : 3-trimethylpyrazole (1-methylantipyrine) (compare Knorr, Abstr., 1906, i, 893). The corresponding sulphur compound, 2 : 5-*sulphido*-1 : 2 : 3-*trimethylpyrazole*,



obtained by the action of sodium sulphide on the methiodide or methochloride, contains $1{\cdot}5H_2O$, which it loses at 100—105°; when anhydrous it has m. p. 147°, and hydrated, m. p. 83°.

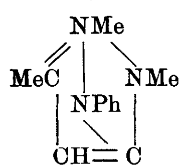
The *hydrochloride*, $C_6H_{10}N_2S,HCl$, forms large prisms, which deliquesce in the air; the *platinichloride*, $(C_6H_{10}N_2S)_2H_2PtCl_6$, forms a reddish-brown, amorphous powder, which decomposes at 320°; the *hydriodide* forms slender needles, m. p. 168°.

4-*Bromo*-2 : 5-*sulphido*-1 : 2 : 3-*trimethylpyrazole*, $C_6H_9N_2BrS$, prepared from the methiodide of 5-chloro-4-bromo-3-methylpyrazole, crystallises in colourless needles, m. p. 221°. The *trioxide*,

$$C_6H_{10}O_3N_2S,$$

can be prepared by passing chlorine into an aqueous solution of sulphido-1 : 2 : 3-trimethylpyrazole, or by the action of sodium sulphite on the methiodide of 5-chloro-1 : 3-dimethylpyrazole, and crystallises in colourless needles, m. p. 227° (decomp.). The thiopyrine combines with methyl iodide at the ordinary temperature, yielding the *methiodide*, $NMeI<^{NMe\text{---}}_{CMe\cdot CH}>C\cdot SMe$, as pale yellow, compact crystals, m. p. 199°; the corresponding *methochloride* contains $2H_2O$, and has m. p. 130°; the *platinichloride* forms golden-yellow needles, m. p. 225°. When the thiopyrine or its methiodide is distilled, the ψ-compound, 5-*methylthiol*-1 : 3-*dimethylpyrazole*, $N<^{NMe\text{---}}_{CMe-CH}>C\cdot SMe$, is obtained as a colourless oil, b. p. 243°; its *platinichloride* crystallises in golden-yellow plates, m. p. 264°, and its *nitroso*-derivative, $N<^{NMe\cdot C\cdot SMe}_{CMe\cdot C\cdot NO}$, forms dark green, glistening needles. When oxidised with permanganate in acetic acid solution, the ψ-compound yields a *sulphone*, $C_6H_{10}O_2N_2S$, as colourless, glistening needles, m. p. 121°.

2 : 5-*Anilo*-1 : 2 : 3-*trimethylpyrazole* (1-*methylanilopyrine*), annexed formula, obtained by heating the methiodide or methochloride of chlorodimethylpyrazole with aniline at 124° for two hours, forms compact crystals, m. p. 82°; it is strongly alkaline, and rapidly absorbs carbon dioxide. The *hydrochloride*, $C_{12}H_{16}N_3Cl,2H_2O$, forms compact, colourless needles, m. p. 238° when anhydrous; the *platinichloride* forms golden-yellow needles, m. p. 207°; the *picrate*, $C_{12}H_{16}N_3,C_6H_3O_7N_3$, yellow prisms, m. p. 129°; the *chromate*, $(C_{12}H_{15}N_3)_2,H_2Cr_2O_7$, orange-yellow plates, m. p. 171°, and the *carbonate*, $C_{12}H_{15}N_3,H_2CO_3$, a colourless powder, m. p. 102° (decomp.). The *methiodide*, $NMeI<^{NMe\text{---}}_{CMe\cdot CH}>C\cdot NMePh$, forms slender, colourless needles, m. p. 200°, and the *propiodide*,

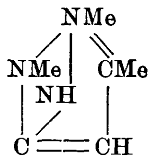


$$C_{12}H_{15}N_3,C_3H_7I,$$

compact crystals, m. p. 176°. When the methiodide is distilled under reduced pressure it yields the ψ-compound, 5-*methylanilino*-1 : 3-*dimethylpyrazole*, $N<^{NMe\text{---}}_{CMe\cdot CH}>C\cdot NMePh$, as a viscid, colourless oil, b. p. 165°/30 mm. Its *nitroso*-derivative, $C_{12}H_{14}ON_4$, forms dark green, compact crystals, m. p. 135°. When the hydrochloride is distilled under 30 mm. pressure, it yields methyl chloride and 5-*anilino*-1 : 3-*dimethylpyrazole*, $N<^{NMe\text{---}}_{CMe\cdot CH}>C\cdot NHPh$, m. p. 95°.

2 : 5-*Imino*-1 : 2 : 3-*trimethylpyrazole* (1-*methyliminopyrine*), annexed

formula, obtained by heating 5-chlorodimethylpyrazole methochloride with aqueous ammonium hydroxide at 130°, forms a yellow oil, and yields a *hydrochloride* in the form of slender needles, m. p. 258°. The *aurichloride*, $C_6H_{11}N_3,HAuCl_4$, forms golden-yellow plates, m. p. 184°; the *platinichloride*, yellow needles, m. p. 210°. The base absorbs carbon dioxide rapidly. J. J. S.



1 : 2-Dimethoxyphenanthraphenazine. ILIE J. PISOVSCHI (*Ber.*, 1910, **43**, 2137—2144).—1 : 2-Dimethoxyphenanthraphenazine,

$$C_6H_2(OMe)_2<\begin{matrix}N:C\cdot C_6H_4\\ | \quad\; |\\ N:C\cdot C_6H_4\end{matrix},$$

has been synthesised from acetylvanillin by the following series of reactions: $CHO\cdot C_6H_3(OMe)\cdot OAc \longrightarrow CHO\cdot C_6H_2(OMe)(NO_2)\cdot OAc \longrightarrow$ $CHO\cdot C_6H_2(OMe)(NO_2)\cdot OH \longrightarrow CHO\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow$ $CO_2H\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow$ $NH_2\cdot CO\cdot C_6H_2(OMe)_2\cdot NO_2 \longrightarrow NH_2\cdot C_6H_2(OMe_2)_2\cdot NO_2 \longrightarrow$ $C_6H_2(\underset{1:2}{NH_2})_2(\underset{3:4}{OMe})_2 \longrightarrow C_6H_2(OMe)_2<\begin{matrix}N:C\cdot C_6H_4\\ | \quad\; |\\ N:C\cdot C_6H_4\end{matrix}.$

A modification of Pschorr and Sumuleanu's method for the preparation of acetylvanillin (Abstr., 1900, i, 178) is described. *adj*-*o*-Nitroveratraldehyde is best prepared by methylating *o*-nitrovanillin with methyl sulphate and alkali; it has m. p. 63°, and when oxidised in acetone solution with aqueous permanganate yields *o*-nitroveratric acid, m. p. 203°.

The *chloride*, $NO_2\cdot C_6H_2(OMe)_2\cdot COCl$ [2 : 3 : 4 : 1], forms slender, colourless needles, m. p. 73°, and the *amide*, $NO_2\cdot C_6H_2(OMe)_2\cdot CO\cdot NH_2$, crystallises from toluene in long, colourless needles, m. p. 172°, and is resistent towards hydrolysing agents.

(adj)-3-*Nitro*-4-*aminoveratrole*, $NO_2\cdot C_6H_2(OMe)_2\cdot NH_2$, crystallises in red needles, m. p. 74°, and exhibits dichroism. When reduced with iron and acetic acid, it yields adj-*veratrylenediamine*, $C_6H_2(NH_2)_2(OMe)_2$, in silver-white plates, m. p. 97°. This base is much more stable than Moureu's *s*-veratrylenediamine (Abstr., 1897, i, 411). The halide salts form colourless needles, but their aqueous solutions have a cherry-red or reddish-violet colour. The base condenses with phenanthraquinone in the presence of acetic acid, yielding 1 : 2-*dimethoxyphenanthraphenazine* in yellow, felted needles, m. p. 174—175°. Its dilute solutions have a green fluorescence. The *hydrochloride* and *hydrobromide* are red; the *hydriodide*, brownish-black, and all three are hydrolysed by water. J. J. S.

Products of the Action of the Primary Amines on the Dinitrosacyls [Glyoximeperoxides]. II. JACOB BÖESEKEN (*Rec. trav. chim.*, 1910, [ii], **14**, 275—292. Compare Abstr., 1898, i, 696).—Wieland and Semper have shown (Abstr., 1904, i, 54; 1908, i, 108) that the dinitrosacyls probably have the endoxyfurazan or furoxan, $\begin{matrix}\cdot C - C\cdot \\ \| \quad\; \| \\ N\cdot O\cdot N\end{matrix}>O$, rather than the glyoxime-peroxide configuration, $\begin{matrix}\cdot C:N\cdot O\\ | \qquad\;\; | \\ \cdot C:N\cdot O\end{matrix}$.

The conclusions drawn previously (Abstr., 1898, i, 696) from the

reactions of these compounds are now reconsidered in the light of Wieland and Semper's work.

[With H. Couvert.]—Diphenyldinitrosacyl, prepared by Holleman's method (Abstr., 1893, i, 205), when heated in ethereal solution with *p*-bromoaniline (2 mols.) gives dark brown needles, decomposing at 126°, of *benzoyl*-p-*bromoanilinofurazan*, probably according to the following scheme:

$$\begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}C(COPh)} \\ \quad\ \ \Vert \qquad \Vert \\ \quad\ \mathrm{N\cdot O\cdot N{-\!\!-\!\!-\!\!-}}\end{array}\!\!>\mathrm{O} \longrightarrow \begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}C\cdot NH\cdot C_6H_4Br} \\ \quad\ \ \Vert \qquad \Vert \\ \quad\ \mathrm{N\cdot O\cdot N}\end{array}.$$

If this furazan is heated on a water-bath with glacial acetic acid, it is transformed into an isomeride, which crystallises in colourless, felted needles, m. p. 208°. This isomeride is not attacked by concentrated sulphuric acid or by nitric acid (D 1·35), and, therefore, the presence of the ·CN group is very improbable, but it dissolves in potassium ethoxide solution, giving a golden-yellow liquid, which, on heating on a water-bath, becomes colourless, and yields the *potassium* salt of p-*bromophenylcyanocarbamide*. The free p-*bromophenylcyanocarbamide* forms colourless needles, decomposing above 325°.

The production of a substituted nitrile by intramolecular change has been observed by Claisen (Abstr, 1904, i, 14; 1909, i, 185), by Wieland and Hess (Abstr., 1909, i, 369), by Wolff (Abstr., 1895, i, 192), and by Hantzsch and Urbahn (Abstr., 1895, i, 393). From its resemblance to the reactions described by these authors, the formation of *p*-bromophenylcyanocarbamide probably occurs thus:

$$\underset{\text{(I) Colourless.}}{\begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}N} \\ \quad\ \ \Vert \qquad \Vert \\ \quad\ \mathrm{N\cdot O\cdot C\cdot NH\cdot C_6H_4Br}\end{array}} + \mathrm{NaOH} = \underset{\text{Golden-yellow.}}{\begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}NNa} \\ \quad\ \ \Vert \qquad | \\ \quad\ \mathrm{N\cdot O\cdot C{:}N\cdot C_6H_4Br}\end{array}} + \mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}NNa} \\ \quad\ \ \Vert \qquad | \\ \quad\ \mathrm{N\cdot O\cdot C{:}N\cdot C_6H_4Br}\end{array} + \mathrm{NaOH} = \underset{\text{Colourless.}}{\begin{array}{l}\mathrm{C{-\!\!-}NNa} \\ \equiv \qquad | \\ \mathrm{N\ \ OC\cdot NH\cdot C_6H_4Br}\end{array}} + \mathrm{Ph\cdot CO_2Na}.$$

The author considers that the colourless isomeride obtained from benzoyl-*p*-bromoanilinofurazan has the constitution of *benzoyl*-p-*bromoanilino*-*aβ′*-*furodiazole* (I), and is formed from the furazan by a partial Beckmann change, thus:

$$\begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}C\cdot NH\cdot C_6H_4Br} \\ \quad\ \ \Vert \qquad \Vert \\ \quad\ \mathrm{N\cdot O\cdot N}\end{array} \longrightarrow \begin{array}{l}\mathrm{COPh\cdot C\cdot C\cdot NH\cdot C_6H_4Br} \\ \qquad\quad \Vert \ \ \Vert \\ \quad\ \mathrm{HO\cdot N\ N\cdot OH}\end{array} \longrightarrow$$

$$\begin{array}{l}\mathrm{COPh\cdot C\cdot N} \\ \qquad\quad \Vert \ \ \Vert \\ \mathrm{HO\cdot N\ \ C(OH)\cdot NH\cdot C_6H_4Br}\end{array} \longrightarrow \begin{array}{l}\mathrm{COPh\cdot C{-\!\!-}N} \\ \quad\ \ \Vert \qquad \Vert \\ \quad\ \mathrm{N\cdot O\cdot C\cdot NH\cdot C_6H_4Br}\end{array}.$$

p-Bromophenylcyanocarbamide cannot be recrystallised from water owing to partial decomposition. It is decomposed by dilute hydrochloric acid according to the equation: $C_8H_6ON_3Br + 2H_2O = C_6H_4Br{\cdot}NH_2 + CO_2 + CO(NH_2)_2$. From conductivity measurements, the value $2{\cdot}4 \times 10^{-4}$ was obtained for its dissociation constant (K), whilst a colorimetric comparison (using Congo-red) with hydrochloric acid of different strengths gave $1{\cdot}8 \times 10^{-4}$.

A solution of the potassium salt of *p*-bromophenylcyanocarbamide gives a white, flocculent precipitate with silver nitrate, stable in the light and soluble in ammonia. The ammoniacal solution deposits small, brilliant crystals of the *silver ammonia* derivative, $C_8H_5ON_3BrAg,NH_3$, which are not acted on by light, but lose ammonia when heated.

Addition of a solution of copper sulphate to a solution of potassium *p*-bromophenylcyanocarbamide gives a yellowish-green, crystalline precipitate of the *copper* salt. The latter is a very sensitive reaction for all cyanocarbamides.

When the potassium salt is warmed at 50° with sulphuric acid or hydrogen peroxide (1·5 mols.) and a little potassium hydroxide solution (compare Radziszewski, Abstr., 1885, 496; Peski, Abstr., 1909, i, 647), p-*bromophenylbiuret*, $C_6H_4Br\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2$, is formed, which crystallises in long needles decomposing at 230° (approx.).

Similarly, when heated in a sealed tube at 100° with ammonium sulphide, the potassium salt is converted into p-*bromophenylthiobiuret*, $C_6H_4Br\cdot NH\cdot CO\cdot NH\cdot CS\cdot NH_2$, which crystallises in long, silky needles, soluble in strong alkalis, from which it is precipitated by carbon dioxide. This thiobiuret has an extremely bitter taste, and loses sulphur when treated with ammoniacal silver or copper solutions.

E. H.

Aminophenazines. ALFRED WOHL and MARTIN LANGE (*Ber.*, 1910, **43**, 2186—2188).—2-Aminophenazine,

$$C_6H_4<\begin{matrix} N\cdot C\cdot CH:CH \\ N\cdot C\cdot CH:C\cdot NH_2 \end{matrix},$$

is formed when a mixture of *o*-nitroaniline, aniline hydrochloride, and finely-powdered zinc chloride is heated at 180—185° for half an hour. The same product is formed when formanilide is used in place of aniline hydrochloride. The m. p. of the pure product is 288° (corr.), not 274°.

Aminonaphthaphenazine, obtained by heating *o*-nitroaniline, α-naphthylamine, and zinc chloride at 150—180°, crystallises from xylene in yellowish-brown, glistening prisms, m. p. 294° (decomp.).

When substituted anilines are used instead of aniline or α-naphthylamine, the yields of phenazines are small. J. J. S.

Triazole and Tetrazole from Azoimide. OTTO DIMROTH and GUSTAV FESTER (*Ber.*, 1910, **43**, 2219—2223).—Azoimide reacts with acetylene when heated in acetone solution for seventy hours at 100° in sealed tubes, forming 1 : 2 : 3-triazole, $NH<\begin{matrix} CH:CH \\ N=N \end{matrix}$. This was identified by methylation of the silver salt to 1-*methyl*-1 : 2 : 3-*triazole*, which forms a very characteristic *aurichloride*, m. p. 160°.

Similarly, azoimide combines with hydrogen cyanide when heated for two to three days at 100° in alcoholic solution to form tetrazole, and this affords the best method of preparing tetrazole.

Phenylazoimide combines with acetylene when heated in acetone solution for forty hours to 1-phenyl-1 : 2 : 3-triazole. Phenylazoimide, however, does not condense with hydrogen cyanide or cyanogen, or with ethyl cinnamate. E. F. A.

The Oxidation of Some Azo-derivatives to the Corresponding Azoxy-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 793—795).—Only a few instances of the oxidation of azo- to

azoxy-compounds are described in the literature, and some of these are doubtful.

If hydrogen peroxide is added to a solution of azobenzene in acetic acid, pure azoxybenzene is obtained in a few days. The reaction closely resembles the conversion of tertiary amines into their oxides by the same reagent. This result, taken together with other reactions studied by the author, favours the constitution $\underset{\overset{\Vert}{O}}{R\cdot N{:}N\cdot R}$ for the azoxy-compounds. C. H. D.

Researches on Benzidine Formation. HENRI DUVAL (*Bull. Soc. chim.* 1910, [iv], 7, 727—732. Compare this vol., i, 559, 588).—2 : 2′-*Hydrazodiphenylethane*, $C_6H_4<\begin{matrix}NH-NH\\CH_2\cdot CH_2\end{matrix}>C_6H_4$, prepared by reducing 2 : 2′-azodiphenylethane (Abstr., 1909, i, 747) with zinc dust and barium hydroxide in aqueous alcoholic solution, forms yellowish-white crystals, m. p. 151°, which give only very small quantities of a colourless, nitrogenous, weakly basic, crystalline substance, m. p. 230°, when treated with hydrochloric acid. Like the corresponding methane derivative, 2 : 2′-azodiphenylethane, when reduced with a boiling hydrochloric acid solution of stannous chloride, gives 2 : 2′-diaminodiphenylethane, described by Busch and Weiss (Abstr., 1900, i, 699). The conclusion is drawn that the reactions in the diphenyl, diphenylmethane, and diphenylethane series are essentially different from those in the benzene series, since in the former cases the benzidine transformation does not occur. E. H.

Changes in the Physical Conditions of Colloids. X. Action of Organic Bases and Amphoteric Electrolytes on Albumin. HANS HANDOVSKY (*Biochem. Zeitsch.*, 1910, 25, 510—538. Compare this vol., i, 344).—The influence of bases and amphoteric electrolytes on the formation of albumin salts has been investigated by means of viscosity measurements. The comparative data indicate that the hydrolysis of the albumin salts increases as the dissociation constant of the added base diminishes. From the observations with amphoteric electrolytes it is found that variations of the basic dissociation constant between 10^{-12} and 10^{-15} have little effect on the formation of albumin ions in comparison with variations in the acid dissociation constant. Amphoteric electrolytes with small basic dissociation constant and higher acid dissociation constant are most favourable to the formation of neutral albumin complexes. H. M. D.

General Protein Chemistry. I. The Coagulation of Denatured Albumin, Considered as a Function of the Hydrogen Ion Concentration and of the Salts. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, 27, 38—52).—Experiments were carried out to test the Helmholz-Bredig theory that surface-tension reaches a maximum and precipitation follows most readily when the protein particles carry no charge, that is, are immersed in a liquid of certain definite hydrogen ion concentration. For this purpose, dialysed albumin was denatured by heating. Mixtures of acetic acid and

sodium acetate in varying quantities were added to the turbid mixture, and the mixture producing the optimum sedimentation effect was noted. The hydrogen ion concentration of this solution could be readily determined. The rate of sedimentation varied when salts other than sodium acetate were employed. It was found that the isoelectric constant of serum albumin was 0.3×10^{-5}, and the relative acidity 1.6×10^{3}. The sedimentation rate is, in the first place, a function of the hydrogen ion concentration, and, in the second place, a function of the total content in electrolytes. The sedimentation rate is at a maximum when the $H^{\cdot}$ concentration is that of the isoelectric point, and is larger the poorer the solution is in total electrolytes.

S. B. S.

Hæmocyanin of Limulus polyphemus. CARL ALSBERG and E. D. CLARK (*J. Biol. Chem.*, 1910, **8**, 1—8).—Hæmocyanin does not appear to be uniformly the same substance in all parts of the animal kingdom. That obtained from *Limulus* blood differs from that described by Henze from *Octopus* blood in percentage composition, in its precipitability by dialysis, by full saturation with magnesium sulphate, by half saturation with ammonium sulphate, in not having been crystallised, and in being more readily broken up by acid with liberation of the copper. No copper compound analogous to hæmatin was formed. In its globulin-like characters, the *Limulus* hæmocyanin thus resembles that described by Halliburton, who worked mainly with Crustacean blood. The following table of percentage composition is given:

	C.	H.	N.	S.	Cu.	O.
Octopus	53·66	7·33	16·09	0·86	0·38	21·68
Limulus	48·94	7·10	16·18	1·56	0·28	25·94

W. D. H.

Guanylic Acid. IVAR BANG (*Biochem. Zeitsch.*, 1910, **26**, 293—311).—The protein was prepared by extracting pancreas with hot water and adding oxalic acid to the extract. This was dissolved in potassium hydroxide solution, and to this was added solid ammonium sulphate, so that the solution was $\frac{1}{2}$ to $\frac{2}{3}$ saturated (260 grams of salt to 500 c.c. of solution). The filtrate from the precipitated protein was diluted, and the guanylic acid precipitated from the liquid thus obtained either by copper acetate or copper sulphate and ammonia. The copper salt was decomposed by hydrogen sulphide, and the filtrate from the copper sulphide precipitated by 25% hydrochloric acid and twice the volume of alcohol. The precipitate was washed with water, and as the acid guanylic salt dissolved, acid was added to the washings. Four to five grams of guanylic acid were thus obtained from five organs of an ox. On hydrolysis, this guanylic acid yielded guanine, contaminated by a little xanthine, which the author succeeded in showing was a secondary product formed from the first-named base, phosphoric acid, and a pentose, the quantity of which was estimated by the author's hydroxylamine method, and amounted to 41% of the guanylic acid hydrolysed. The author discusses the formula of guanylic acid and its relationship to inosic and thymonucleic acids

S. B. S.

The Optical Rotation of Gelatin. HANS TRUNKEL (*Biochem. Zeitsch.*, 1910, 26, 493—513).—The optical activity of fresh gelatin solutions is variable, and reaches a maximum between the twelfth and hundred and twentieth hour. On warming, the original activity is restored. The activity is also dependent on temperature, decreasing with increasing temperature to 35°, when a maximum is attained. The optical activity is not proportional to the concentration; the weaker the concentration the smaller is the dextrorotation. The deviation is the smaller the longer and higher the solution is heated before taking the observation. The rotation of β-gelatin is appreciably smaller than that of the α-variety. The combining power for tannin of gelatin diminishes on keeping at first rapidly, and then more slowly; the rotatory power shows the opposite action (increasing rapidly at first, etc.). These phenomena are to be ascribed to a change in the condition known as "hysteresis," which the author discusses.

S. B. S.

The Anti-protease of Yeast Juice. EDUARD BUCHNER and HUGO HAEHN (*Biochem. Zeitsch.*, 1910, 26, 171—198).—It has been already shown that expressed yeast juice when kept loses first the co-enzyme and finally the zymase, which latter cannot be subsequently regenerated on addition of the former. The destruction of the zymase is due to an endotryptase. If boiled juice is added to the zymase, however, it can be preserved from destruction, owing to the fact that the boiled juice contains in addition to the co-enzyme an anti-protease which protects the coagulable proteins from the action of the endotryptase. This anti-protease also protects gelatin from liquefaction by endotryptase, and prevents the digestion of caseinogen by the same ferment. It acts also as an anti-substance to trypsin and pepsin. It is not identical with the co-enzyme, for the latter can be destroyed by heating yeast juice for several hours, or by the action of dilute acids at 100°, or by the action of alkali at 37°; under these conditions the anti-protease remains intact. The authors have not yet succeeded in separating chemically the anti-protease from the co-enzyme. Both are destroyed by lipase. The anti-protease is not a simple acid which inhibits the action of endotryptase, and as the anti-proteolytic action of the boiled juice remains intact after neutralisation, and neither is it a simple amino-acid, as substances do not exert any marked anti-action to endotryptase. Preliminary experiments indicate that it is an organic ester-like substance. The authors draw the conclusion that the anti-protease plays an important part in the life-processes of the yeast. The protective action is probably due to the capacity of the anti-protease to combine with the protein.

S. B. S.

Organic Chemistry.

Catalytic Reactions in the Wet Way, Based on the Use of Aluminium Sulphate. JEAN B. SENDERENS (*Compt. rend.*, 1910, **151**, 392—394).—The addition of sand in the classical method for the preparation of ethylene is usually recommended on the ground that it prevents frothing. The present communication contains details of experiments from which it appears that this material acts as a catalyst and enables the reaction to proceed at a lower temperature. Aluminium sulphate, especially that prepared by calcining ammonium alum, is still more effective in this respect. The proportions recommended are 200 c.c. of a mixture of sulphuric acid (2 vols.), 95% alcohol (1 vol.), and 10 grams of anhydrous aluminium sulphate. Without the latter, the mixture yields no ethylene at 138° ; with sand it gives 7·5—8 c.c. per minute, and with aluminium sulphate, 32 c.c. per minute.

The use of aluminium sulphate is stated to be advantageous in the industrial preparation of ethyl ether. A mixture of sulphuric acid (3 vols.) and 95% alcohol (4 vols.) with 5% of the sulphate gives ether at 110°, the reaction becoming rapid at 130°. In the absence of a catalyst the evolution of ether is not regular until 140°. The method is not suitable with the higher alcohols, the unsaturated hydrocarbon being produced together with liquid condensation products.

Propylene is conveniently prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5% of anhydrous aluminium sulphate at 100—110°. The gaseous product contains 95% of propylene.

W. O. W.

Preparation of Glyceryl Mono- and Di-bromohydrins. P. CARRÉ (*Bull. Soc. chim*, 1910, [iv], 7, 835—836).—Glyceryl α-bromohydrin, b. p. 134°/16 mm., is best prepared by diluting glycerol (200 grams) with water (60 grams), passing in hydrogen bromide (162 grams), warming the mixture in a closed vessel at 100° during five to six hours, and distilling the product under reduced pressure, the fraction boiling at 125—160°/16 mm. being collected and re-distilled. The αγ-dibromohydrin (b. p. 105°/16 mm.) is obtained in a yield of 55 to 60% of the theoretical by warming glycerol (185 grams) to 100°, passing in hydrogen bromide (325 grams), and heating the mixture at 100° during five to six hours. The fraction boiling at 100—120°/16 mm. is collected and re-distilled. Both products are colourless when freshly distilled, but become coloured on exposure to light.

T. A. H.

Solubility of Ethyl Ether in Water. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, **2**, 21—35).—The ether used had b. p. 34·55°/761·2 mm. The relation between the refractive index and the composition of various mixtures of ether and water at 20° was first determined. It was found that the difference (Δ) between the angle of

refraction of water and the solution of ether in water is a linear function of the number of grams (x) of ether contained in 100 grams of the solution, as expressed by the formula $x = 0{\cdot}0946\Delta$.

In order to determine the solubility of ether in water at different temperatures, water was shaken with excess of ether in a tap funnel surrounded by a water jacket. When saturation was complete, the two layers were allowed to separate, and small portions of the lower layer run off into weighed quantities of water contained in stoppered flasks, the quantity of water being so regulated that a homogeneous solution was obtained at 20°. The weights of the separate portions of the lower layer were determined by difference. The angle of refraction of the homogeneous solution was then measured at 20°, and its composition determined by means of the formula given above; the composition of the saturated solution from which it was prepared could then be calculated.

The following results were obtained from the smoothed curve, x being the number of grams of ether dissolved in 100 grams of water in the saturated solution.

Temp. ...	0°	5°	10°	15°	20°	25°	30°
x	13·13	11·18	9·55	8·22	7·08	6·13	5·39

J. S. P.

Preparation of Chloroacetyl Chloride from Dichlorovinyl Ether. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 222194).—When dichlorovinyl ether is saturated with dry hydrogen chloride, kept for twenty-four hours at the ordinary temperature, and then very gradually heated to boiling, *ethyl trichloroethyl ether*, $CH_2Cl{\cdot}CCl_2{\cdot}OEt$, is formed; this on distillation is readily decomposed into ethyl chloride and chloroacetyl chloride (b. p. 105°): $CHCl{:}CCl{\cdot}OEt + HCl \longrightarrow CH_2Cl{\cdot}CCl_2{\cdot}OEt \longrightarrow EtCl + CH_2Cl{\cdot}COCl$.

F. M. G. M.

Preparation of the Anhydrides of Fatty Acids from their Salts. TH. GOLDSCHMIDT (D.R.-P. 222236).—The preparation of aliphatic paraffin anhydrides by treating the salts of the acids with sulphur chloride has previously been described (Abstr., 1903, i, 309); it is now found that the reaction takes place if an intimate mixture of dry powdered sulphur and the sodium (or calcium) salt of the acid is treated with chlorine gas at a temperature of $-24°$ with continual stirring: $8C_2H_3O{\cdot}ONa + S + 6Cl = 6NaCl + Na_2SO_4 + 4(C_2H_3O)_2O$.

The mixture is then kept at the ordinary temperature, warmed to 90°, and subsequently distilled in a vacuum. F. M. G. M.

Preparation of β-Methyladipic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 221849).—The technical preparation of β-methyladipic acid may be conveniently carried out by oxidising 4-methyl*cyclo*hexanol with boiling concentrated nitric acid to 4-methyl*cyclo*hexanone; this intermediate product is then treated with potassium permanganate in alkaline solution, separated from hydrated manganese oxide, and the solution acidified, when a good yield of β-methyladipic

is obtained; it finds employment in the preparation of dyes and in pharmacology. F. M. G. M.

Preparation of Organic Aluminium Compounds. ERNST SCHLIEMANN'S EXPORT-CERESIN-FABRIK (D.R.-P. 221888).—Aluminium salts of mineral waxes may be obtained by treating the raw or purified waxes with aluminium salts, metallic aluminium, or aluminium hydroxide in the presence of an alkali, the function of which is to hydrolyse the esters of the fatty acids; the aluminium may combine with one, two, or three equivalents of the acid. A salt obtained from a pure wax containing 70% wax acid yielded an *aluminium montanate* of deep yellow colour, m. p. 93—95°, and giving a clear solution in hot petroleum. These compounds are employed as preservatives. F. M. G. M.

Preparation of Ammonium Hydrogen *l*-Tartrate. ANDRÉ KLING (*Bull. Soc. chim.*, 1910, [iv], 7, 774—776).—In connexion with the author's process for the estimation of tartaric acid as calcium racemate (this vol., ii, 359), a process for the preparation of ammonium hydrogen *l*-tartrate, based on the observations of Holleman (Abstr., 1898, i, 515; ii, 545) and Marckwald (Abstr., 1896, i, 207), is described. Ordinary tartaric acid is racemised by boiling it with sodium hydroxide solution, and the resulting racemic acid precipitated as the calcium salt. From this, racemic acid is regenerated, and the *l*-acid separated by means of cinchonine. From the cinchonine salt, the *l*-acid is recovered as ammonium hydrogen tartrate in the usual way, and freed from a trace of *d*-acid by fractional precipitation with calcium acetate, until the precipitate formed consists solely of crystals of calcium *l*-tartrate. The filtrate on concentration furnishes crystals of the desired salt. Illustrations of the crystals of calcium *l*-tartrate and racemate are given. T. A. H.

Ozo-salts of Titanium. ARRIGO MAZZUCHELLI and ENRICO PANTANELLI (*Gazzetta*, 1910, **40**, i, 666—682. Compare Abstr., 1909, i, 631).—The complex potassium ozotitanotartrate previously described (*loc. cit.*) crystallises with $9H_2O$, not with $10H_2O$, as there stated owing to a printer's error in the original paper. R. V. S.

Preparation of Acraldehyde. JEAN B. SENDERENS (*Compt. rend.*, 1910, **151**, 530—532. Compare this vol, i, 649).—Anhydrous or hydrated aluminium sulphate effects the catalytic dehydration of glycerol at 105—110°, producing acraldehyde. The large amount of potassium hydrogen sulphate commonly employed in the preparation of this substance from glycerol is unnecessary, since the salt acts as a catalyst. By heating 250 grams of glycerol with 10 grams of potassium hydrogen sulphate for three hours at a temperature not exceeding 110°, 130—140 c.c. of liquid are obtained, which, on re-distillation, furnishes 34—38 c.c. of acraldehyde. The yield is somewhat smaller than that obtained in the usual way, but the product is more stable, and polymerises less rapidly. W. O. W.

Action of Acetic Anhydride and Its Homologues on Organo-magnesium Compounds. H. FOURNIER (*Bull. Soc. chim.*, 1910, [iv], **7**, 836—840).—Grignard and Tissier have shown (Abstr., 1901, i, 316) that tertiary alcohols are formed by the action of acetic or benzoic anhydride on magnesium methyl iodide. The author has found, in addition, that ketones are produced in this reaction (*Bull. Soc. chim.*, 1904, [iii], **31**, 483; 1906, [iii], **35**, 19), and a detailed account of his results are now given.

The anhydride (1 mol.) is dissolved in ether, and to this the magnesium alkyl haloid (1 mol.) is added drop by drop, the mixture being cooled in a bath of ice and salt and continuously agitated. The mixture is set aside during two to three hours, and then poured into ice-cold water. The ethereal extract of this is then shaken with dilute sodium hydroxide solution. The purified ethereal solution contains (1) the ketone formed, (2) the ester corresponding to the acid anhydride employed, and the alkyl radicle of the magnesium compound used, and (3) sometimes the tertiary alcohol. The last is separated by fractional distillation, and the ester is eliminated from the residue by hydrolysis, the alcohol formed being distilled off. The ketone is finally isolated by adding water, extracting with ether, drying the solution, and fractionating. The chief reactions occurring are represented by the following equations: $(R\cdot CO)_2R + R'MgBr = R\cdot CO\cdot O\cdot CRR'\cdot O\cdot MgBr + H_2O = MgBr\cdot OH + R\cdot CO_2H + R\cdot CO\cdot R'$.

With magnesium ethyl bromide, acetic anhydride yields methyl ethyl ketone; with magnesium *iso*butyl chloride, methyl *iso*butyl ketone, and with magnesium *iso*amyl bromide, methyl *iso*amyl ketone. The reaction has also been investigated for propionic, butyric, *iso*butyric, *iso*propylacetic, and heptoic anhydrides with various magnesium alkyl haloids, and the corresponding ketones prepared and identified, usually by means of their semicarbazones. T. A. H.

Preparation of Methylene Ketones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 222551).—The action of formaldehyde on ketones in the presence of alkaline condensing agents yields keto-alcohols, which by the action of condensing agents, such as zinc chloride, sulphuric acid, or sodium hydrogen sulphate, are converted into methylene ketones.

Methyleneacetone, $COMe\cdot CH:CH_2$, b. p. 80°, under the ordinary pressure is prepared by heating ketobutanol (100 parts) with zinc chloride (2 parts). It is a colourless, highly refractive oil with a pungent odour.

Methylenemethyl ethyl ketone, $CH_2:CH\cdot COEt$, a colourless oil with a strong odour, b. p. 96°, is similarly prepared. These compounds are employed in pharmacy. F. M. G. M.

Action of Ultra-violet Light on Certain Carbohydrates. HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1910, **151**, 316—318).—Under the influence of light from a quartz-mercury lamp, lævulose undergoes profound decomposition when in aqueous solution, carbon monoxide, carbon dioxide, formaldehyde, and methyl alcohol having been recognised amongst the products. The reaction proceeds more readily in a vacuum than when air is present.

Aldoses do not appear to undergo this degradation. Glycerol and mannitol after exposure to the rays acquire reducing properties.

W. O. W.

Degradation Experiments with Carbohydrates. CARL NEUBERG and ELSE HIRSCHBERG (*Biochem. Zeitsch.*, 1910, **27**, 327—338).—Attempts were made to prepare *l*-glyceraldehyde. The method employed was to degrade *l*-arabonic acid to *l*-erythrose by the ferric acetate and hydrogen peroxide method of Ruff and Meusser, to oxidise the latter to *l*-erythronic acid by bromine water, and to obtain *l*-glyceraldehyde from the latter both by the ferric acetate and hydrogen peroxide oxidation, and by Neuberg's method by the electrolytic decomposition of the copper salt. The experiments were made possible by the authors' discovery of an easy method for preparing *l*-arabonic acid. Cherry gum was hydrolysed by dilute sulphuric acid, which was then removed. The *l*-arabinose thus formed was not isolated, but the quantity in solution was directly estimated polarimetrically, and then sufficient bromine was added to oxidise it to *l*-arabonic acid, which was then isolated as a calcium salt. On oxidising this to *l*-erythrose, an acid by-product insoluble in alcohol was isolated, and obtained in the form of a brucine salt, which was apparently *l*-$\alpha\beta\gamma$-trihydroxybutyrylformic acid, $CO_2H\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$. On attempting to prepare *l*-glyceraldehyde from erythronic acid by both methods mentioned, an analogous *l*-$\alpha\beta$-dihydroxypropionylformic acid was also probably formed. Only traces of a glyceraldehyde could be isolated, however, and this was optically inactive. S. B. S.

Influence of Boric Acid on the Inversion of Sucrose by the Catalytic Action of Hydrochloric Acid. KATSUNOSUKE ARAFURU (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, **2**, 229—236).—Boric acid acts as a positive catalyst on the inversion of sucrose. Löwenthal and Lenssen (*J. pr. Chem.*, 1862, **85**, 401) found that it retards the catalytic action of hydrochloric acid, but the author finds that it increases the catalytic action. When the concentration of the hydrochloric acid is kept constant, the accelerating effect of the boric acid increases with its concentration, whereas the influence of the boric acid on the catalytic action of hydrochloric acid is practically independent of the concentration of the latter acid. T. S. P.

Constitution of Vicianose: Diastatic Hydrolysis. GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1910, **151**, 325—327. Compare this vol., i, 156).—Vicianose, the new sugar from *Vicia angustifolia*, has been hydrolysed by emulsin, and found to furnish dextrose and arabinose in equimolecular proportions. It may therefore be regarded as a disaccharide formed by the union of these two substances. W. O. W.

New Observations on Callose. LOUIS MANGIN (*Compt. rend.*, 1910, **151**, 279—283. Compare Abstr., 1890, i, 734).—The tissue of *Bornetina corium*, a coriaceous cryptogram, is a substance having the same composition as cellulose, but differing from it in its insolubility in

Schweitzer's reagent and its behaviour towards iodine. Sulphuric acid hydrolyses it with formation of dextrose. From these and other observations the author considers it to consist of practically pure callose.

Like cellulose, callose is met with in different states of aggregation, probably corresponding with different degrees of polymerisation. Tanret's fongose (Abstr., 1898, i, 154) is supposed to be identical with callose. W. O. W.

Relations of Callose with Fongose. CHARLES TANRET (*Compt. rend.*, 1910, **151**, 447—449. Compare preceding abstract).—The author denies the identity of callose with fongose (fungose). Callose is insoluble in aqueous alkali hydroxides, but becomes soluble after treatment with dilute sulphuric acid, as described in connexion with the preparation of fongose. Callose appears to be a more complex substance than fongose, and the relation between the two compounds appears to be similar to that existing between starch and amylose. W. O. W.

Celluloses. I. WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1910, 587—589).—On macerating filter paper with concentrated hydrochloric acid at 28°, no reducing substance is produced even after forty hours. If the paper is macerated during sixty-two hours and the mixture then heated at 95—96° during twenty minutes, it becomes brown, but the filtrate does not reduce Fehling's solution. The brownish residue is partly soluble in ammonia, and consists of humic matter. Cotton macerated during forty hours in hydrochloric acid shows no reduction, but after eighty-seven hours at 28·5°, and then ten minutes at 95—96°, shows copious reduction. It dissolves in fuming hydrobromic acid at 29° in a few minutes, and the solution blackens on keeping. Such a solution gives a slight, brownish-black precipitate, partly soluble in ammonia on dilution, and reduces Fehling's solution. T. A. H.

Cellulose. I. Hydrocellulose. H. JENTGEN (*Zeitsch. angew. Chem.*, 1910, **23**, 1541—1546).—Hydrocellulose is formed by the action of water vapour on cellulose containing adsorbed acid, the acid acting as a contact catalyst. For the formation of the adsorption product between acid and cellulose, it is necessary that the former be in the so-called molecular condition, that is, dissolved in a non-dissociating medium, such as glacial acetic acid, amyl acetate, ether, etc. The acids generally used are hydrochloric and sulphuric, and also their salts with weak bases, and the velocity of hydrolysis depends on the medium used, of which glacial acetic acid is the best.

Hydrocellulose is not extremely resistent towards acids and bases. At medium concentrations, sulphuric acid causes amyloid formation, stronger acid dissolves it, and the most concentrated acid destroys it. It is soluble in zinc chloride, phosphoric acid, fuming nitric acid, and concentrated ammoniacal copper oxide, in the last-named to 10—15%; it is only very sparingly soluble in Wright's liquid.

Alkalis readily attack hydrocellulose, oxycellulose being formed at

the boiling point. It dissolves in cold sodium hydroxide to the extent of about one-third, the remainder being mercerised. The solution contains hemi-cellulose, which can be precipitated by acids, and also yellow to brown degradation products, which are soluble in water.

T. S. P.

Colloidal Properties of Starch, Especially its Electrical Transport. FILIPPO BOTTAZZI and C. VICTOROFF (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 7—14. Compare Fouard, Abstr., 1908, i, 953; Maquenne and Roux, *ibid.*, 1906, i, 547).—The authors confirm the results of the above-named writers. The amylose of starch forms a colloidal solution with water, which is perfectly clear and transparent, but does not dialyse. The solution can be filtered through hardened gelatin under pressure (ultra-filtration). When an electric current is passed through it, no migration is observed. The amylopectin of starch forms with water a suspension, in which the granules are visible under the ultra-microscope. The suspension is the more stable the more alkali it contains, so that dialysis, which removes a part of the alkali, causes a partial precipitation. The solution is precipitated by acids. When subjected to ultra-filtration, the substance does not pass through the gelatin, and thus a separation from amylose can be effected. The two substances can also be separated by precipitating the amylopectin with acid, the amylose being afterwards thrown down by the addition of alcohol to the filtrate. Amylopectin is transported towards the anode in neutral solutions containing only small quantities of electrolytes; when large quantities of the latter are present, or when the solution is alkaline or acid, no transport takes place.

R. V. S.

Action of (1) Hydracids, (2) Hydrolysing Agents, on Starch. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 515—517, 586—587).—A mixture of starch (3 grams), water (35—40 grams), and concentrated hydrochloric acid (2 c.c.) kept at 14° reduces Fehling's solution slightly after three days and markedly after six days. The action is much more rapid at 100°. Concentrated hydrobromic or hydriodic acid behaves similarly on being kept in contact with starch at the ordinary temperature, and hydrolysis is also effected by hot dilute hydriodic acid.

The following substances dissolved, or suspended, in water also hydrolyse starch: ferric, platinic, auric, and stannous chlorides; chlorine; potassium ferrocyanide, ferricyanide, dichromate, and hydroxide; sodium hydroxide, hydrogen carbonate, and dichromate; ammonium, lithium, barium, strontium, and calcium hydroxides; cupric sulphate; cobalt nitrate; nitric (dilute), chromic (dilute), acetic, tartaric, benzoic, picric, and other organic acids.

T. A. H.

Synthesis of Agmatine. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1910, **68**, 170—172. Compare this vol., i, 500).—Agmatine has been synthesised by the following process. Carbon dioxide is passed for fourteen days through a suspension of silver cyanamide in a

solution of tetramethylenediamine hydrochloride. The liquid is acidified with sulphuric acid, filtered, and the filtrate mixed with an aqueous solution of silver sulphate until a test portion gives a dark brown precipitate with barium hydroxide. The whole is then neutralised with barium hydroxide, filtered, and the filtrate saturated with barium hydroxide. The dark brown precipitate is washed with water, suspended in dilute sulphuric acid, decomposed with hydrogen sulphide, and the resulting sulphate transformed into the sparingly soluble carbonate.

Agmatine can also be obtained by the direct action of an aqueous solution of cyanamide on tetramethylenediamine, and its constitution as aminobutyleneguanidine, $NH_2\cdot C(NH)\cdot NH\cdot [CH_2]_4\cdot NH_2$, is confirmed. J. J. S.

Attempts to Synthesise $\alpha\epsilon$-Diaminopentan-γ-ol. Otto Morgenstern and Ernst Zerner (*Monatsh.*, 1910, **31**, 777—780).—With the object of preparing large quantities of $\alpha\epsilon$-diaminopentan-γ-ol, it was sought to convert *s*-dichlorohydrin by means of potassium cyanide into the dinitrile, $OH\cdot CH(CH_2\cdot CN)_2$, and reduce this compound. Dichlorohydrin (1 mol.) and potassium cyanide (2 mols.) were caused to interact in various ways, but the nitrile was only obtained as a blackish-brown, amorphous, hygroscopic solid, which could not be purified. On hydrolysis, glutaconic acid was obtained, of which the *copper* salt forms a bluish-green, crystalline powder, becoming brown at 250°. Reduction of the crude nitrile by means of sodium and amyl alcohol gave a small quantity of a colourless distillate with an amine-like odour, b. p. 255—270°. *Diaminopentanol picrate*,

$$C_5H_{14}ON_2,2C_6H_3O_7N_3,$$

decomposes at 272°. E. F. A.

Synthesis of Polypeptides. XXXII. (I) Derivatives of Aspartic Acid. Emil Fischer and Albert Fiedler (*Annalen*, 1910, **375**, 181—198. Compare Abstr., 1909, i, 887).—In view of the importance of aspartic acid as a constituent of natural proteins, the authors have applied to it the reactions by which glycylglutamyldiglycine was synthesised from glutamic acid (Fischer, Kropp and Stahlschmidt, Abstr., 1909, i, 368), and have succeeded in preparing a tetrapeptide from 3 mols. of glycine and 1 mol. of aspartic acid, to which the name *glycylaspartyldiglycine* is assigned.

Chloroacetyl-l-*aspartic acid*, $CH_2Cl\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, prepared from chloroacetyl chloride and aspartic acid or asparagine under suitable conditions, is a crystalline powder, which has m. p. 142—143° (decomp., corr.), and $[\alpha]_D^1$ 4·19° in aqueous solution, and yields with 25% ammonium hydroxide after three days at the ordinary temperature, *glycyl*-l-*aspartic acid*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, m. p. 207° (decomp., corr.), $[\alpha]_D^{20}$ 11·08° in aqueous solution, which crystallises with $1H_2O$. d-α-*Bromo*iso*hexoylglycyl*-l-*aspartic acid*, $CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, prepared from glycyl-*l*-aspartic acid and *d*-α-bromo*iso*hexoyl chloride, is hygroscopic, has m. p. 119—120° (corr.), $[\alpha]_D^{21}$ 61·35° in alcoholic solution, separates from hot water in short prisms containing $\frac{1}{2}H_2O$,

and by treatment with ammonium hydroxide as above is converted into l-*leucylglycyl*-l-*aspartic acid*,
$CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$,
m. p. 239° (decomp., corr.), and $[\alpha]_D^{20}$ 55·10° in aqueous solution.

Chloroacetylaspartic acid is treated with acetyl chloride and phosphorus pentachloride in the cold, and an ethereal solution of the resulting crude acid chloride is treated with ethereal ethylglycine at 0°, whereby ethylglycine hydrochloride and *ethyl chloroacetylaspartyldiglycine*,
$CH_2Cl \cdot CO \cdot NH \cdot CH(CO \cdot NH \cdot CH_2 \cdot CO_2Et) \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$,
are obtained; after the removal of the former by cold water, the latter is purified by hot ethyl acetate and animal charcoal. It separates in colourless needles, has m. p. 176—177° (corr.), and is optically inactive, racemisation having occurred probably during the conversion of the chloroacetylaspartic acid into its chloride. *Chloroacetylaspartyldiglycine*, m. p. 142—143° (decomp., corr.), obtained by hydrolysing the preceding ester with *N*-sodium hydroxide at the ordinary temperature, separates from hot water in crystals containing H_2O, is sparingly soluble in cold water, has a strongly acid reaction, and is converted by 25% ammonium hydroxide at 25° in five days into *glycylaspartyldiglycine*,
$NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO \cdot NH \cdot CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$,
m. p. 201—203° (corr.), an aqueous solution of which becomes dark blue when boiled with copper oxide.

d-*α-Bromo*iso*hexoyl*-l-*aspartic acid*,
$$CHMe_2 \cdot CH_2 \cdot CHBr \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H,$$
m. p. 150° (corr.), $[\alpha]_D^{22}$ 8·10° in aqueous solution, is prepared from aspartic acid and *d*-*α*-bromo*iso*hexoyl chloride, and is converted by ammonium hydroxide into l-*leucyl*-l-*aspartic* acid, m. p. 182° (decomp., corr.), $[\alpha]_D^{18}$ 26·92° in aqueous solution, which separates from hot water in slender needles containing $2H_2O$. C. S.

Synthesis of Polypeptides. XXXII. (II.) Dipeptides of Serine. EMIL FISCHER and HANS ROESNER (*Annalen*, 1910, **375**, 199—206).—As mixed polypeptides of serine are probably formed by the partial hydrolysis of silk-fibroin, the authors have prepared certain dipeptides of serine which it is hoped may be of use in elucidating the nature of the hydrolytic products of silk-fibroin. The reaction between *r*-serine and chloroacetyl chloride in *N*-sodium hydroxide cooled by a freezing mixture leads to the formation of *chloroacetylserine*,
$$CH_2Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot OH,$$
m. p. 122—123° (corr.), which tastes and reacts strongly acid, and is converted by 25% ammonium hydroxide at the ordinary temperature into *glycyl*-dl-*serine*, m. p. 207° (decomp., corr.), which has a slight acid reaction and gives a deep blue colour when its aqueous solution is warmed with copper oxide. *Glycyl*-dl-*serine anhydride*,
$$OH \cdot CH_2 \cdot CH <^{NH \cdot CO}_{CO \cdot NH}> CH_2,$$
m. p. 227° (corr.), is obtained by saturating a cold methyl-alcoholic suspension of glycylserine with hydrogen chloride and treating the

product in concentrated methyl-alcoholic solution with methyl alcohol saturated with ammonia at 0°.

By similar methods, *a-bromopropionylserine*,

$$CHBrMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot OH,$$

m. p. 143° (decomp., corr.), i-*alanylserine*,

$$NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot OH,$$

m. p. 209—214° (decomp., corr.), and i-*alanylserine anhydride*,

$$OH\cdot CH_2\cdot CH<\begin{matrix}NH\cdot CO\\CO\cdot NH\end{matrix}>CHMe,$$

m. p. 228° (corr.), have been obtained. C. S.

Syntheses of Hydroxybetaines. I. Synthesis of β-Trimethyl-a-lactobetaine. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1910, **68**, 1—11).—Attempts have been made to synthesise hydroxybetaines, as compounds of this type, for example, carnitine, novaine, reducto-novaine, and oblitine, occur in nature.

The *basic hydriodide* of *β-trimethyl-a-lactobetaine*, $C_{12}H_{27}O_6N_2I$, is formed when *iso*serine (Fischer and Leuchs, Abstr., 1902, i, 269) is dissolved in a 7·5% solution of sodium hydroxide in methyl alcohol, mixed with methyl iodide, and the resulting sodium salt decomposed with hydriodic acid. It crystallises from 96% alcohol in compact, transparent prisms, m. p. 198—200°. The *sodium* salt,

$$C_{12}H_{26}O_6N_2INa,$$

crystallises from 96% alcohol in slender, glistening needles, m. p. 203—206°. The basic *hydrochloride*, $C_{12}H_{27}O_6N_2Cl$, obtained by the action of silver chloride on an aqueous solution of the hydriodide, crystallises in slender needles, m. p. 200°. The normal *hydriodide*, $C_6H_{14}O_3NI$, has m. p. 78—80°, and when crystallised from alcohol yields the basic salt. The normal *hydrochloride*, $C_6H_{14}O_3NCl$, has m. p. 155—158°; the *platinichloride*, $C_{12}H_{28}O_6N_2PtCl_6$, crystallises from 50% alcohol. *β-Trimethyl-a-lactobetaine*,

$$NMe_3<\begin{matrix}CH_2\cdot CH\cdot OH\\ \quad\;\; | \\ O\text{——}CO\end{matrix},$$

forms hygroscopic needles, m. p. 203° (decomp.).

The *platinichloride* of the ethyl ester,

$$[NMe_3Cl\cdot CH_2\cdot CH(OH)\cdot CO_2Et]_2PtCl_4,$$

crystallises from aqueous alcohol in hexagonal prisms, which decompose at 235°.

Trimethylamine and β-chlorolactic acid yield carbon dioxide, acetaldehyde, and trimethylamine hydrochloride. J. J. S.

Cheirolin, the Thiocarbimide in Wall-flower Seeds. Its Synthesis and Degradation. WILHELM SCHNEIDER (*Annalen*, 1910, **375**, 207—254. Compare Abstr., 1909, i, 118, 826).—A better method than Wagner's (Abstr., 1908, i, 202) for the isolation of cheirolin from wall-flower seeds is described. The finely ground seeds are extracted with ether, which removes the greater part of the oily constituents, but only a trace of cheirolin. The seeds are then covered with ether, and shaken with 5% sodium carbonate. The cheirolin is thereby liberated and dissolved by the ether. The ethereal extract is evaporated, and the residue is dissolved in 0·5%

sulphuric acid at 50—60°; the acid solution, after being filtered, is treated with ammonium sulphate, the cheirolin is extracted with ether, and is obtained almost pure by evaporating the ethereal solution after it has been dried with potassium carbonate. The seeds of *Cheiranthus cheiri* yield 1·6—1·7%, and those of *Erysimum arkansanum*, 1·3%.

Cheirolin, $C_5H_9O_2NS_2$, m. p. 47—48°, b. p. 200°/3 mm., separates from ether in large, colourless, odourless, prismatic plates, $a:b:c=0·9418:1:0·6228$. Wagner (*loc. cit.*) described it as an alkaloid, but it is entirely without basic properties. The two atoms of sulphur have different functions in the molecule, one being easily oxidised to sulphuric acid, the other only with difficulty. The decomposition of cheirolin by warm dilute acids or alkalis is that of a thiocarbimide, hydrogen sulphide, carbon dioxide, and a primary base, $C_4H_{11}O_2NS$, being obtained quantitatively. This supposition is confirmed, not only by the formation of thiocarbamides with ammonia and amines, but also by the production of the same thiocarbamide from cheirolin and aniline, and from phenylthiocarbimide and the base, $C_4H_{11}O_2NS$; by desulphurisation with mercuric oxide, this thiocarbamide yields a carbamide identical with Wagner's cheirol. The base, $C_4H_{11}O_2NS$, does not contain hydroxyl; the presence of a sulphone group is indicated by the firmness with which the sulphur is bound, the saturated character and insolubility in ether of the base, its stability to hydrochloric acid at 200°, hydriodic acid, and cold potassium permanganate. Boiling potassium permanganate converts the base into an acid, $C_3H_7O_2S·CO_2H$, and fuming nitric acid at 200° produces a good yield of methylsulphonic acid; these two reactions indicate the presence of $·CH_2·NH_2$ and of ·SMe respectively. Consequently, the base is probably

$$SO_2Me(C_2H_4)·CH_2·NH_2,$$

and cheirolin a methylsulphone derivative of propylthiocarbimide, $SO_2Me·CH_2·CH_2·CH_2·NCS$, the methylsulphone group being in the γ-position because the substance is optically inactive. The correctness of these views has been proved synthetically. *Methyl-γ-bromopropylsulphone*, $SO_2Me·CH_2·CH_2·CH_2Br$, m. p. 34°, b. p. 156—158°/1 mm., obtained by treating an alcoholic solution of sodium methylmercaptide at 0° with an alcoholic solution of αγ-dibromopropane and oxidising the resulting sulphide with potassium permanganate, is converted by potassium thiocyanate into the *thiocyanate*,

$$SO_2Me·CH_2·CH_2·CH_2·SCN,$$

m. p. 57°, but all attempts to convert it into the isomeric thiocarbimide have been unsuccessful. The synthesis of cheirolin has been achieved therefore by the following process. *Methyl γ-phthaliminopropyl sulphide*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N·CH_2·CH_2·CH_2·SMe$, m. p. 59—60°, obtained from alcoholic sodium methylmercaptide and γ-bromopropylphthalimide, yields by hydrolysis *methyl γ-aminopropyl sulphide*, b. p. 170° (*hydrochloride*, m. p. 136°; *oxalate*, decomp. 208°; *picrate*, m. p. 126—127°; *picrolonate*, m. p. 184—185°), the hydrochloride of which is oxidised, best by permanganic acid, to *methyl γ-aminopropylsulphone*, the derivatives of which are identical with those of the primary base obtained by the hydrolysis of cheirolin; for

example, the *hydrochloride*, m. p. 146°, *platinichloride*, decomposing at 234°, *di-γ-methylsulphonepropylthiocarbamide*, m. p. 125—126°. The synthetic methyl γ-aminopropylsulphone is finally converted into cheirolin by Hofmann's method with carbon disulphide.

The following compounds have also been prepared: Methyl γ-aminopropylsulphone forms, in addition to the derivatives mentioned above, a *picrate*, m. p. 190—192°, *picrolonate*, m. p. 216°, an N-*benzoyl* derivative, m. p. 102°, is oxidised by boiling potassium permanganate to *methylsulphonepropionic acid*, $SO_2Me\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 105°, and is converted by an excess of methyl iodide into *trimethyl-γ-methylsulphonepropylammonium iodide*, $SO_2Me\cdot[CH_2]_3\cdot NMe_3I$, m. p. 150—152°. Methyl γ-aminopropyl sulphide reacts with an alcoholic solution of cheirolin to form the *thiocarbamide*,

$$SMe\cdot[CH_2]_3\cdot NH\cdot CS\cdot NH\cdot[CH_2]_3\cdot SO_2Me,$$

m. p. 59°, with alcoholic carbon disulphide to form ultimately *di-γ-methylthiopropylthiocarbamide*, $CS[NH(CH_2)_3\cdot SMe]_2$, m. p. 55—56°, and with sodium methoxide and an excess of methyl iodide to form the NS-*dimethiodide* of methyl γ-dimethylaminopropylsulphide,

$$CH_3\cdot S(MeI)\cdot[CH_2]_3\cdot NMe_3I,$$

decomposing at 246°, and also the N-*methiodide*, decomposing at 217°.

An alcoholic solution of cheirolin is converted by alcoholic ammonia into *γ-methylsulphonepropylthiocarbamide*,

$$SO_2Me\cdot[CH_2]_3\cdot NH\cdot CS\cdot NH_2,$$

m. p. 116°, by alcoholic aniline into *γ-methylsulphonepropylphenylthiocarbamide*, $SO_2Me\cdot[CH_2]_3\cdot NH\cdot CS\cdot NHPh$, m. p. 136° (which is also obtained from phenylthiocarbimide and methyl γ-aminopropylsulphone), and by alcoholic methyl γ-aminopropylsulphone into s-*di-γ-methylsulphonepropylthiocarbamide*, $CS(NH\cdot[CH_2]_3\cdot SO_2Me)_2$, m. p. 125—126°, which is also obtained by desulphurising an aqueous solution of cheirolin at 50—60° with mercuric oxide ($\frac{1}{2}$ mol.). s-*Di-γ-methylsulphonepropylcarbamide*, m. p. 172°, is obtained by the action of mercuric oxide on the preceding thiocarbamide, or of an excess of mercuric oxide on a boiling aqueous solution of cheirolin. C. S.

Effect of Pressure and Temperature on Cyanogen. E. BRINER and A. WROCZYNSKI (*Compt. rend.*, 1910, **151**, 314—316. Compare this vol., ii, 557, 707).—The conversion of cyanogen into paracyanogen, which takes place at about 310° under ordinary pressure, can be brought about at lower temperatures by increasing the pressure; thus, at 220° and 300 atmospheres, the gas undergoes a diminution in volume of 10%, and then contains 16% of free nitrogen. Polymerisation also occurs in the neighbourhood of the critical temperature and pressure, but probably not with sufficient rapidity to vitiate determinations of these constants. W. O. W.

Formation of *o*-Nitrotoluene from 2:4-Dinitrotoluene. MORITZ KOHN (*Monatsh.*, 1910, **31**, 745—746. Compare Abstr., 1909, i, 561).—*o*-Nitrotoluene is formed by boiling 2:4-dinitrotoluene with an aqueous alkaline solution of hydroxylamine. No trace of the formation of *p*-nitrotoluene could be detected. E. F. A.

Dinitro-*p*-xylenes. Jan J. Blanksma (*Chem. Weekblad*, 1910, 7, 727—730).—Preparation of the three isomeric nitro-*p*-xylenes by an indirect method has established the fact that it is possible to separate the pure compounds from the mixture resulting from the nitration of *p*-xylene, although only a small proportion of the 2 : 3- and 2 : 5-compounds is obtained.

On reduction with ammonium sulphide, 2 : 3-dinitro-*p*-xylene yields *p*-xylidine-3-sulphonic acid, probably due to replacement of one nitro-group by SH, followed by intramolecular oxidation and the addition of one molecule of water. A. J. W.

Higher Homologues of Benzene. Erling Schreiner (*J. pr. Chem.*, 1910, [ii], 82, 292—296).—The following compounds are produced by the Grignard and the Friedel-Craft reactions. β-Chloro-β-methylpentane, b. p. 110—113°, D_4^{15} 0·8678, $n_D^{16·5}$ 1·41476, yields with benzene and aluminium chloride *β-phenyl-β-methylpentane*, CMe_2Pr^aPh, b. p. 205—206°, D_4^{10} 0·8796, $n_D^{16·5}$ 1·49554. *β-Chloro-βδ-dimethylpentane*, $CHMe_2·CH_2·CMe_2Cl$, b. p. 126—127°, D_4^{10} 0·8650, $n_D^{16·5}$ 1·42015, prepared from the corresponding carbinol, is converted into *β-phenyl-βδ-dimethylpentane*, b. p. 218°, D_4^{15} 0·8741, $n_D^{16·5}$ 1·49383. γ-Chloro-γ-methylpentane, b. p. 116°, D_4^{14} 0·8893, $n_D^{16·5}$ 1·42315, yields *γ-phenyl-γ-methylpentane*, b. p. 204—206°, D_4^{15} 0·8773, $n_D^{16·5}$ 1·49724. Triethylcarbinol forms *γ-chloro-γ-ethylpentane*, CEt_3Cl, b. p. 143—144°, D_4^{25} 0·8644, n_D^{25} 1·43276, which is converted into *γ-phenyl-γ-ethylpentane*, b. p. 220—222°, D_4^{25} 0·8656, n_D^{25} 1·49211. C. S.

The Ditolylmethane from Formaldehyde and Toluene. Otto Fischer and Hans Gross (*J. pr. Chem.*, 1910, [ii], 82, 231—237).—The large residue obtained in the preparation of ditolylmethane from methylal or paraformaldehyde and toluene (Abstr., 1909, i, 563) yields β-methylanthracene by further distillation. When the residue is distilled under diminished pressure, it yields a further quantity of ditolylmethane and a mobile, colourless liquid with a feeble, blue fluorescence, b. p. 247—250°/12 mm., which is apparently a polymeride of ditolylmethane. When the condensation of toluene and paraformaldehyde or methylal in the presence of sulphuric acid is performed at −15° to −10°, only a little ditolylmethane is obtained, the chief product being an amorphous powder.

The ditolylmethane obtained by the authors' process (and also that prepared by Weiler's method) must contain a little *op*-ditolylmethane, because it does not solidify in ice and salt, melts at −3°, and yields β-methylanthracene by distillation over pumice in a red-hot tube; the pure dipara-substance solidifies in ice and salt, melts at 22—23°, and does not yield β-methylanthracene on distillation.

The dinitroditolylmethane obtained by Weiler by the nitration of ditolylmethane is identical with that prepared from *o*-nitrotoluene, formaldehyde, and concentrated sulphuric acid, and must therefore be 3 : 3′-dinitrodi-*p*-tolylmethane; by reduction, it yields the corresponding *diamino*-compound, $C_{15}H_{18}N_2$, m. p. 72—74°, which forms a *diacetyl* derivative, m. p. 264°. C. S.

Ditolylethane and Ditolylethylene from Paraldehyde and Toluene. OTTO FISCHER and L. CASTNER (*J. pr. Chem.*, 1910, [ii], 280—288).—Continuing a former research (O. Fischer, this Journ., 1875, 154), the authors show that the best condition for the production of ditolylethane is to add slowly paraldehyde to a vigorously stirred mixture of concentrated sulphuric acid and toluene at $-20°$, the temperature being kept below $-15°$; after three to four hours the temperature is slowly increased to 0°, and the mass added to water at 0°. When cold toluene is added to a mixture of pure sulphuric acid and paraldehyde at $-20°$, and after three to four hours the temperature is raised to 10° and the mass poured into water, the ditolylethane contains 25—33% of di-*p*-tolylethylene, which is separated by fractional distillation. The di-*p*-tolylethylene and the di-*p*-tolylethane obtained from it by reduction with sodium and alcohol do not yield β-methylanthracene when passed over pumice in a red-hot tube. By bromination in carbon disulphide at 0°, di-*p*-tolylethylene yields an unstable additive compound, which loses hydrogen bromide during its purification, ω *bromodi-*p*-tolylethylene*, $C_{16}H_{15}Br$, m. p. 53—54°, being obtained.

The formation of di-*p*-tolylethylene may be due to the intermediate production of crotonaldehyde, since under the conditions mentioned above this aldehyde, toluene, and sulphuric acid produce the unsaturated hydrocarbon. C. S.

Action of Iodine on *m*-Toluidine. HENRY L. WHEELER (*Amer. Chem. J.*, 1910, 44, 126—145).—It has been shown by Wheeler and Liddle (this vol., i, 17, 19) that when *p*-toluidine is treated with iodine, both mono- and di-iodo-derivatives are produced, whilst with *o*-toluidine, the mono-derivative only is obtained. A study has now been made of the behaviour of *m*-toluidine towards iodine, and the 6-iodo-, 4:6-di-iodo-, and 2:4:6-tri-iodo-derivatives have been isolated. It is probable that small quantities of isomeric compounds, such as the 4-iodo- and 2:6-di-iodo-derivatives, are also formed. When *m*-toluidine (1 mol.) is mixed with iodine (two or three atoms) in presence of ether, water, and calcium carbonate, the product consists of mono- and di-iodo-toluidines, together with some of the original base. When the proportion of iodine is increased to four atoms, a mixture of the mono-, di-, and tri-iodo-derivatives is obtained, in which the di-derivative predominates, whilst with six atoms of iodine, tri-iodo-*m*-toluidine and resinous material are produced.

[With CHARLES HOFFMAN.]—6-Iodo-*m*-toluidine has m. p. 37—39°, instead of 98—99° as stated by Artmann (Abstr., 1905, i, 879). 6-*Iodo-3-acetylaminobenzoic acid*, $NHAc\cdot C_6H_3I\cdot CO_2H$, m. p. 210°, obtained by the oxidation of 6-iodoaceto-*m*-toluidide with potassium permanganate, forms long, colourless, prismatic needles. An attempt was made to prepare 6-iodo-3-aminobenzoic acid by the hydrolysis of the acetyl derivative, but the acid is very unstable, and could not be isolated. 4:6-*Di-iodo-*m*-toluidine*, $NH_2\cdot C_6H_2MeI_2$, m. p. 73—74°, crystallises in large, stout, colourless needles; the *hydrochloride* and *sulphate* were prepared; the *acetyl* derivative, m. p. 213°, forms long, slender, colourless needles, and is only slightly oxidised by potassium permanganate solution even when heated with it in a sealed tube

at 200°. 2 : 4 : 6-*Tri-iodo*-m-*toluidine*, $NH_2\cdot C_6HMeI_3$, m. p. 135°, crystallises in long, pale brown, hair-like needles; the *acetyl* derivative has m. p. 265°. By the action of potassium iodide on the diazotisation product of 2 : 4 : 6-tri-iodo-*m*-toluidine, 2 : 3 : 4 : 6-*tetraiodotoluene*, m. p. 170°, is produced, which forms long needles.

[With CHARLES A. BRAUTLECHT.]—2 : 6-*Di-iodo-aceto*-m-*toluidide*, $C_6H_2MeI_2\cdot NHAc$, m. p. 171°, obtained by the action of iodine chloride on 2-iodoaceto-*m*-toluidide, forms colourless prisms. On hydrolysis, it is converted into 2 : 6-*di-iodo*-m-*toluidine*, m. p. 88°, which crystallises in colourless needles and prisms; the *hydrochloride* was prepared. 2 : 3 : 6-*Tri-iodotoluene*, m. p. 80·5°, prepared by the action of potassium iodide on the diazotisation product of 2 : 6-di-iodo-*m*-toluidine, forms colourless needles.

When a mixture of 6-nitro-*o*-toluidine (1 mol.) and iodine (1 mol.) with ether, water, and calcium carbonate is warmed for several hours, 5-*iodo*-6-*nitro*-o-*toluidine*, $NO_2\cdot C_6H_2MeI\cdot NH_2$, m. p. 85°, is produced, which forms yellow prisms. By the action of potassium iodide on the diazotisation product of this base, 2 : 5-*di-iodo*-6-*nitrotoluene*,

$$NO_2\cdot C_6H_2MeI_2,$$

m. p. 105°, is obtained, which forms colourless needles, and, on reduction, is converted into 3 : 6-*di-iodo*-o-*toluidine*, $NH_2\cdot C_6H_2MeI_2$, m. p. 86°, which crystallises in colourless needles. On treating the diazotisation product of 3 : 6-di-iodo-*o*-toluidine with potassium iodide, 2 : 3 : 6-tri-iodotoluene is obtained in a yield of 90%. When 5-iodo-6-nitro-*o*-toluidine is diazotised in dilute sulphuric acid solution and the product is decomposed with sodium hydroxide and distilled with steam, 3-*iodo*-2-*nitrotoluene*, m. p. 65°, is obtained, which forms colourless, prismatic plates.

[With SAMUEL R. SCHOLES.]—When 4-iodo-3-nitrotoluene is reduced with ferrous sulphate and ammonia, 4-iodo-*m*-toluidine is produced, which has m. p. 38—38·5°, and not 48° as stated by Willgerodt and Simonis (Abstr., 1906, i, 156); the *phenylthiocarbamide* derivative, $C_6H_3MeI\cdot NH\cdot CS\cdot NHPh$, has m. p. 162—163°. 4-Iodoaceto-*m*-toluidide has m. p. 151°, instead of 145—146° as given by Willgerodt and Simonis (*loc. cit.*), and is converted by iodine chloride into 4 : 6-di-iodoaceto-*m*-toluidide. By the action of iodine on 4-iodo-*m*-toluidine, 4 : 6-di-iodo-*m*-toluidine is produced. 3 : 4 : 6-*Tri-iodotoluene*, m. p. 119—120°, obtained by diazotising 4 : 6-di-iodo-*m*-toluidine and treating the product with potassium iodide, forms long, slender, brown needles.

When 3-nitro-*p*-toluidine is warmed with iodine chloride and glacial acetic acid, 5-*iodo*-3-*nitro*-p-*toluidine*, m. p. 98°, is obtained, which crystallises in golden-brown needles, and yields an acetyl derivative, m. p. 202—203°, identical with that obtained by Wheeler and Liddle (this vol., i, 18) by the action of nitric acid on 3-iodoaceto-*p*-toluidide. By diazotising 5-iodo-3-nitro-*p*-toluidine and treating the product with potassium iodide, 4 : 5-*di-iodo*-3-*nitrotoluene*, m. p. 84—85°, is produced, which forms rectangular, orange prisms, and on reduction is converted into 4 : 5-*di-iodo*-m-*toluidine*, m. p. 66—67°, which forms a mass of colourless, slender needles, and yields an *acetyl* derivative, m. p. 183—184°.

5-*Iodo*-3-*nitrotoluene*, m. p. 77°, obtained by the action of potassium iodide on the diazotisation product of 5-nitro-*m*-toluidine, forms yellow, rectangular prisms. On reduction, it is converted into 5-*iodo*-m-*toluidine*, m. p. 78—78·5°, which crystallises in long, colourless needles; the *acetyl* derivative has m. p. 183°. E. G.

[Preparation of 5-Nitro-*m*-anisidine.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 222062).—5-*Nitro*-m-*anisidine*,

$OMe{\cdot}C_6H_3(NH_2){\cdot}NO_2$,

orange-yellow needles, m. p. 120°, is prepared by the reduction of 3 : 5-dinitroanisole, m. p. 105°; the 3-*nitroanisole*-5-*azo*-β-*naphthol* obtained when it is diazotised and coupled with β-naphthol can be employed for the preparation of lakes. F. M. G. M.

Condensation of Some Primary Aromatic Amines with Chloralaniline. STROUD JORDAN (*J. Amer. Chem. Soc.*, 1910, **32**, 973—977).—It is well known that when an amine (1 mol.) is treated with an aldehyde (1 mol.) an additive compound is produced, whilst if the reagents are in the proportion of 2 mols. of the amine to 1 mol. of the aldehyde, a condensation product is formed and water (1 mol.) is eliminated. The experiments now described show that, in certain cases, the additive compound is an intermediate step in the formation of the condensation product, and that it can be converted into the latter on the addition of an excess of free amine.

When an alcoholic solution of freshly prepared chloralaniline is heated with aniline, the condensation product, $CCl_3{\cdot}CH(NHPh)_2$, is obtained.

If chloralaniline is heated with 3-nitro-*p*-toluidine dissolved in benzene, a condensation product, $CCl_3{\cdot}CH(NHPh){\cdot}NH{\cdot}C_6H_3Me{\cdot}NO_2$, m. p. 98—99°, is obtained, which forms a yellow, crystalline mass, and is difficult to purify owing to the facility with which it decomposes with production of 5-chloro-3-nitro-*p*-toluidine. E. G.

Preparation of Optically Active *o*-Dihydroxyphenylalkylamines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 222451. Compare this vol., i, 372).—It is found that the synthetic optically inactive racemic *o*-dihydroxyphenylalkylamines can be resolved by means of optically active tartaric acids; by this method, *l*-β-3 : 4-trihydroxyphenylethylmethylamine, identical with the therapeutically important base, *l*-adrenaline, has been obtained. Racemic β-3 : 4-trihydroxyphenylethylmethylamine (50 parts) is treated with *d*-tartaric acid (43 parts) in either aqueous or alcoholic solution, the solvent removed under reduced pressure, and the residue dried; it is then stirred with methyl alcohol in which *l*-trihydroxyphenylethylmethylamine *d*-tartrate is insoluble, this is crystallised from a mixture of methyl and ethyl alcohols (when pure it has m. p. 149°), and on treatment with alkali yields *l*-adrenaline, m. p. 211—212°. The methyl-alcoholic extract yields the more soluble *d*-trihydroxyphenylethylmethylamine. If *l*-tartaric acid is employed, the *d*-base *l*-tartrate is obtained as the most insoluble component of the mixture. Other racemic dihydroxyphenylalkylamines can be similarly resolved into their active components. F. M. G. M.

Unsymmetrical Aromatic Derivatives of Oxamide. H. Suida, jun. (*Monatsh.*, 1910, **31**, 583—616).—A number of unsymmetrical disubstituted oxamides of the type of phenyltolyloxamide have been prepared by the action of arylamines on ethyl oxanilate and ethyl *p*-tolyloxamate at about 150—200°. The products, with the exception of those which contain para-substituents in both benzene nuclei, give Tafel's reaction with dichromate and concentrated sulphuric acid (Abstr., 1892, 709). The products of hydrolysis of most of the compounds have been examined (compare Dyer and Mixter, Abstr., 1887, 251). Phenyl-*p*-tolyloxamide has m. p. 204—205° (compare Heller, Abstr., 1904, i, 730). *Phenyl*-o-*tolyloxamide*,

$$NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me,$$

crystallises in microscopic prisms, m. p. 176—177°, and is rather more readily soluble than the para-compound. *Phenyl*-m-*tolyloxamide* crystallises from 60% alcohol in long, colourless, glistening needles, m. p. 168°. All three compounds when boiled with aqueous alcoholic potassium hydroxide yield a mixture of oxanilic and a tolyloxamic acid. With moderately dilute alkali and boiling for about two hours, oxalic acid does not appear to be formed.

Phenyl-p-*xylyloxamide*, $NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_3Me_2$ [$Me_2 : NH = 1 : 4 : 2$], forms microscopic needles, m. p. 196—197°; the isomeric *meta*-compound [$Me_2 : NH = 1 : 3 : 4$] has m. p. 200—202°.

Phenyl-ψ-cumyloxamide, $NHPh\cdot CO\cdot CO\cdot C_6H_2Me_3$, has m. p. 202—203° when crystallised from alcohol, but 215—217° when crystallised from acetone. p-*Tolyl*-p-*xylyloxamide*, $C_6H_4Me\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_3Me_2$, crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 168°. *Phenyl-α-naphthyloxamide*,

$$NHPh\cdot CO\cdot CO\cdot NH\cdot C_{10}H_7,$$

crystallises from alcohol in prismatic needles, m. p. 191—192°, and the isomeric *β-naphthyl* derivative forms a crystalline powder from benzene and has m. p. 227—228°. *Phenyl*-p-*nitrophenyloxamide*, $NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2$, crystallises from ethyl acetate in yellowish-grey needles, m. p. 251—252°. *Phenyl*-o-*nitro*-p-*tolyloxamide*, $NHPh\cdot CO\cdot CO\cdot C_6H_3Me\cdot NO_2$ [$Me : NO_2 : NH = 1 : 3 : 4$], crystallises from alcohol in glistening, golden-yellow plates, m. p. 188—190°.

When phenyl-*p*-tolyloxamide is heated on the water-bath for fifteen minutes with nitric acid (D 1·4), it yields the *o*-mononitro-derivative, m. p. 182—183° and soluble in ethyl acetate, together with the 4 : 2'-*dinitro*-compound, $C_{15}H_{12}O_6N_4$, insoluble in ethyl acetate, but crystallising from chloroform in yellow, glistening needles resembling pyrites. The constitution of the two nitro-derivatives was established by an examination of the products of hydrolysis; in the case of the dinitro-compound these were oxalic acid, *p*-nitroaniline, and 3-nitro-*p*-toluidine.

Nitric acid and iodine transform phenyl-*p*-tolyloxamide into the p-*iodo*-derivative, $C_6H_4I\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me$; this crystallises in microscopic prisms, which are still solid at 280°.

Most of the diarylated oxamides when hydrolysed with dilute alcoholic potassium hydroxide yield an oxamic acid and arylamine; the hydrolysis does not, as a rule, proceed to the formation of oxalic acid. In most cases both the reactions $NHR\cdot CO\cdot CO\cdot NHR' + H_2O \longrightarrow$

$NHR\cdot CO\cdot CO_2H + NH_2R'$ and $NHR\cdot CO\cdot CO\cdot NHR' + H_2O \longrightarrow NH_2R + CO_2H\cdot CO\cdot NHR'$ proceed at the same time, so that the final product consists of a mixture of the two substituted oxamic acids and of the two amines. The formation of the two acids was proved by preparing and analysing a mixture of the silver salts of the two acids. In the case of the β-naphthyl, *o*-nitro-*p*-tolyl, and *p*-nitrophenyl derivatives of oxanilide, only one acid is formed, namely, oxanilic. J. J. S.

Alkylation of Aromatic Amino-acids. III. Aminomethylbenzoic Acids. HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1910, **44**, 113—126).—It has been shown in an earlier paper (this vol., i, 381) that when the salts of *o*-, *m*-, and *p*-aminobenzoic acids are treated with alkyl halides, alkylaminobenzoic acids are produced, but that certain amino-acids which have negative atoms or groups adjacent to the amino-group yield esters under these conditions. It was therefore considered of interest to ascertain whether a similar influence is exerted by substituents which are not usually regarded as having a negative character, such as the methyl group. A study has therefore been made of the ethylation of 4-amino- and 2-amino-mesitylenic acids, and it has been found that the former yields an ester, whilst the latter yields the diethylamino-acid (30 parts), the ethylamino-derivative (10 parts), and the ester (1 part). The investigation has been extended to the ethylation of 4-amino-*m*-toluic acid and 5-iodo-4-amino-*m*-toluic acid. The former gives the ethylamino-derivative (15 parts), the diethylamino-derivative (1 part), and a small quantity of another substance, probably the ester (2 parts). 5-Iodo-4-amino-*m*-toluic acid does not readily undergo alkylation; it yields the ester (15 parts) and the diethylamino-acid (4 parts). These results show that the different behaviour of amino-acids cannot be fully explained either by the theory of stereochemical interference or by the positive or negative character of the substituents.

Ethyl 4-*aminomesitylenate*, m. p. 67°, crystallises in colourless plates.

2-*Diethylaminomesitylenic acid*, m. p. 98°, forms colourless, prismatic crystals, and gives a sky-blue fluorescence in solution in light petroleum. 2-*Ethylaminomesitylenic acid*, m. p. 190° (decomp.), crystallises in large, colourless prisms.

4-Nitro-*m*-toluic acid was prepared by the nitration of *m*-toluic acid. An isomeric acid is simultaneously produced, which has been found to be 6-nitro-*m*-toluic acid. The acid obtained by Jacobsen (Abstr., 1882, 185) in this reaction, and supposed to be the 4-nitro-derivative, was doubtless a mixture, as was also the amino-product obtained on reduction. 6-*Nitro*-m-*toluamide*, m. p. 190°, forms large, transparent prisms. 4-*Ethylamino*-m-*toluic acid*, m. p. 71—72°, crystallises in large, transparent prisms, and dissolves in light petroleum to form a solution with a sky-blue fluorescence. 4-*Diethylamino*-m-*toluic acid*, m. p. 55—57°, forms long, slender needles.

5-*Iodo*-4-*amino*-m-*toluic acid*, m. p. 212° (decomp.), crystallises in square plates. The *ethyl* ester, m. p. 70—71°, forms long, colourless

prisms. *5-Iodo-4-diethylamino-*m*-toluic acid,* m. p. 125—126°, forms fine, hair-like crystals. E. G.

Preparation of Carbamino-acid Esters from 6-Amino-α-naphthol-3-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 221967).—The carbamino-acid alkyl or alkylaryl esters of 6-amino-α-naphthol-3-sulphonic acid (J acid) of the general formula $SO_3H\cdot C_{10}H_5(OH)\cdot NH\cdot CO_2R$ (R = alkyl or alkylaryl group) can be readily prepared by slowly dropping the required alkyl chlorocarbonate into an aqueous solution of the sodium salt of the above acid at the ordinary temperature and with continual stirring.

Sodium 6-ethylcarbamino-α-naphthol-3-sulphonate is readily soluble in water, the *barium* salt sparingly so.

Sodium 6-amylcarbamino-α-naphthol-3-sulphonate is sparingly soluble in water, and the solution readily gelatinises.

Sodium 6-benzylcarbamino- and *6-nitrobenzylcarbamino-α-naphthol-3-sulphonates* are sparingly soluble in water. F. M. G. M.

Acyl Derivatives of Thioamides. MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōtō,* 1909—1910, 2, 241—244).—Thiobenzamide and thio-*p*-toluamide when dissolved in benzene react with acid chlorides with the formation of nitrogen-substituted compounds of the constitution $R\cdot CS\cdot N(OCR')_2$ or $R\cdot CS\cdot N{<}^{CO}_{CO}{>}R''$. The reaction takes place at the ordinary temperature, occasional cooling being necessary. The resulting compounds are stable towards hydrochloric acid, but easily decomposed by alkalis or by reducing agents, hydrogen sulphide being one of the decomposition products in both cases.

Phthalylthiobenzamide, $C_6H_5\cdot CS\cdot N{:}C_2O_2{:}C_6H_4$, crystallises from benzene in stout violet plates containing half a molecule of benzene of crystallisation. From alcohol, it crystallises in scales, and from ether in prisms, and has m. p. 126°. *Phthalylthio-*p*-toluamide,*

$$C_7H_7\cdot CS\cdot N{:}C_2O_2{:}C_6H_4,$$

forms violet scales or needles, m. p. 179°. *Succinylthio-*p*-toluamide,* $C_7H_7\cdot CS\cdot N{:}C_2O_2{:}C_2H_4$, forms violet, needle-shaped crystals, m. p. 142°. *Acetylthiobenzamide,* $Ph\cdot CS\cdot NAc_2$, forms red plates, m. p. 94—95°. *Acetylthio-*p*-toluamide,* $C_7H_7\cdot CS\cdot NAc_2$, crystallises in red plates, m. p. 121—123°. T. S. P.

Diguaiacylphosphoric Acid. PIERRE DUPUIS (*Bull. Soc. chim.,* 1910, [iv], 7, 846—847. Compare Abstr., 1908, i, 529; this vol., i, 248).—On adding phosphoric anhydride to guaiacol and heating to 110°, a mixture of mono- and di-guaiacylphosphoric acids is formed, from which the former may be separated by neutralisation with sodium carbonate solution and precipitation with copper sulphate. From the filtrate, diguaiacylphosphoric acid separates on adding hydrochloric acid, and can be recrystallised from boiling water. The *potassium* salt is isomorphous with the sodium salt (*loc. cit.*), and crystallises with 1 mol. H_2O. T. A. H.

Preparation of Hexa- and Penta-methylphloroglucinol. JOSEF HERZIG and BR. ERTHAL (*Monatsh.,* 1910, 31, 827—831).—The

methylation in the nucleus of phloroglucinol and orcinol (Herzig and Wenzel, Abstr., 1906, i, 93) is a complicated reaction, and the yield is dependent on factors which are still imperfectly understood.

Hexamethylphloroglucinol could not be prepared by Spitzer's method (Abstr., 1890, 1110), but both hexa- and penta-methyl derivatives are obtained on warming phloroglucinol in aqueous alkaline solution with methyl iodide until the reaction is neutral. The hexamethyl derivative crystallises out, and the pentamethyl derivative is extracted from the residue with ether. The yield is satisfactory, but the relative proportions of the two products vary in the different experiments. The pentamethyl derivative can be further methylated to hexamethylphloroglucinol by the same treatment in aqueous solution, a transformation which does not take place in alcohol.

Pentamethylphloroglucinol is converted by the action of diazomethane into the methyl ether, m. p. 52—55°, which was previously known as a viscid oil obtained by the action of methyl iodide and potassium hydroxide. E. F. A.

Some Cyclic Ethylenic Ethers and their Bromo-derivatives. G. Busignies (*Compt. rend.*, 1910, **151**, 515—517).—The Grignard reaction proceeds much more readily with substituted alkyloxy-aromatic ketones than with the alkylamino-ketones studied previously (Abstr., 1909, i, 736). Phenyl phenetidyl ketone yields in this way *phenyl*-p-*phenetidylethylene*, m. p. 71°, *phenyl*-p-*phenetidylpropylene*, m. p. 54°, and p-*phenetidylstilbene*, m. p. 93°.

The bromination of phenyl-*p*-anisylethylene has been studied, but the author has been unable to obtain the isomeric monobromo-derivatives described by Stoermer and Simon (Abstr., 1905, i, 53). Compounds of this class containing the grouping CH_2:C: yield only dibromo-derivatives even in the cold, whilst those containing the grouping ·CH:C: furnish monobromo-derivatives with liberation of hydrogen bromide. Phenyl-*p*-anisylethylene gives a *dibromo*-derivative, $C_{15}H_{14}OBr_2$, m. p. 115°; the corresponding compound from phenyl-*p*-phenetidylethylene has m. p. 90°. *β-Bromo-α-phenyl*-p-*phenetidylpropylene* has m. p. 48°. *β-Bromo-α*-p-*phenetidylstilbene*, m. p. 73°, forms a *dibromo*-derivative, $C_{22}H_{18}OBr_2$, m. p. 150°. *β-Bromodi*-p-*phenetidylpropylene* has m. p. 60°. W. O. W.

Catalytic Preparation of Mixed Ethers from Alcohols and Phenols. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1910, **151**, 359—362. Compare this vol., i, 294, 456, 536).—Phenol (1 vol.) and methyl alcohol (1·5 vols.) in the state of vapour are passed over a column of thorium oxide at 390—420°. The products are fractionated, and the middle portion washed with sodium hydroxide solution. Anisole is thus obtained in excellent yield after a single rectification. Under the same conditions, *m*-cresol gives a very good yield of the methyl ether, but with the para-compound the yield is less satisfactory. The method is successful with 2 : 4-xylenol, thymol, carvacrol, *β*-naphthol, and *α*-naphthol. In the latter case the catalyst is kept at about 400°, and the yield is 33%.

Ethers were not obtained from dihydric phenols owing to the

formation of stable compounds with the thorium oxide, these being slowly decomposed with formation of complex products.

The homologues of anisole are obtained with less ease owing to the readiness with which the higher alcohols undergo dehydration. The reaction, however, offers an advantageous means of preparation if the phenol is dissolved in excess of the alcohol. The ethyl, propyl, and *iso*amyl ethers of phenol, and *p*-tolyl ethyl ether were prepared in this way. W. O. W.

Catalytic Preparation of Phenylic and Diphenylic Ethers. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, **151**, 492—494. Compare preceding abstract).—Diphenyl oxide and its homologues are readily prepared by passing the vapour of a phenol over thorium oxide at 390—450°. Solid phenols may be dissolved in benzene before vaporisation. The catalytic method gives a yield of 50% of the oxide in the case of phenol and *p*- and *m*-cresol. With *o*-cresol, however, a higher temperature is necessary and the yield is poor.

When the reaction is allowed to proceed at a higher temperature, hydrogen is liberated and a diphenylene oxide produced. In the case of phenol and *p*-cresol, considerable quantities of the condensed oxides are formed at 475°; *m*-cresol under these conditions gives rise to m-*ditolylene oxide*, $C_{14}H_{14}O$, brilliant lamellæ, m. p. 182°. The analogous *ortho*-compound has m. p. 121°. W. O. W.

Scission of Phenolic Ethers by Organo-magnesium Compounds. VICTOR GRIGNARD (*Compt. rend.*, 1910, **151**, 322—325. Compare Abstr., 1904, i, 494).—Organo-magnesium derivatives do not react with phenolic ethers under ordinary conditions. By adding magnesium, however, to a mixture of an alkyl bromide with anisole or phenetole in equimolecular proportions, employing benzene as the solvent, reaction occurs. Hydrolysis of the product in the usual way regenerates the phenolic ether, but if the solvent is removed and the residue gradually heated to 150—160° under 10—15 mm., only half the ether is recovered, the remainder having undergone conversion into phenol. Under the same conditions, estragole gave a 50% yield of *p*-allylphenol. In the case of safrole, fission takes place at the temperature of the water-bath, but the unstable dihydroxy-derivative cannot be isolated. A small quantity of a substance, probably 2-methoxy-5-allylphenol, is also produced.

The foregoing results are explained by supposing that an oxonium complex is first produced by addition, and that this undergoes scission, yielding the compound OPh·MgBr, and probably ethylene and a saturated hydrocarbon.

The results obtained by Schorigin by the action of alkyl derivatives of sodium with ethers may be explained in the same way (this vol., i, 547). W. O. W.

Action of Bromine in Presence of Aluminium Bromide on Phenyl Ethers. A. BONNEAUD (*Bull. Soc. chim.*, 1910, [iv], **7**, 776—781).—Bodroux has shown (Abstr., 1898, i, 641) that in the case of phenols, bromine in excess in presence of aluminium bromide

(1) displaces all the hydrogen atoms in the nucleus; (2) leaves unchanged lateral chains of the type $\cdot CH_2R$, and (3) destroys lateral chains attached to the nucleus by ⁝CH or ⁞C, replacing each of these by one atom of bromine. The author shows that the same rules hold good in the case of phenyl alkyl ethers, and that in addition these ethers undergo saponification and regenerate the corresponding phenols, except in the case of ethers containing two aromatic nuclei; thus, under these conditions, anisole, phenetole, and phenyl propyl ether all yield pentabromophenol, diphenyl ether furnishes *decabromodiphenyl ether*, colourless prisms, m. p. 293°, whilst the methyl and ethyl ethers of *o*-, *m*-, and *p*-cresols and the methyl and ethyl ethers of thymol and carvacrol all give the corresponding tetrabromocresols. The following new compounds were prepared by the action of the appropriate alkyl iodide on the potassium derivative of pentabromophenol, *pentabromoanisole*, m. p. 174°, *pentabromophenetole*, m. p. 136°, and *pentabromophenyl propyl ether*, m. p. 98°. T. A. H.

The Cholesterol Group. VIII. *iso*Cholesterol. A. MORESCHI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 53—57. Compare this vol., i, 317, and Darmstädter and Lifschütz, Abstr., 1898, i, 245).—Along with coprosterol and hippocoprosterol (Dorée and Gardner, Trans., 1908, 1625; Abstr., 1908, ii, 514), *iso*cholesterol belongs to the group of the hydrosterols. To obtain it, wool fat is repeatedly extracted with boiling alcohol, the residue is subjected to saponification, and the unsaponified portion is fused for some hours in contact with an excess of benzoic anhydride. The mixture of cholesteryl benzoate and *iso*cholesteryl benzoate obtained is purified by means of boiling alcohol, and by precipitation from ether with alcohol. The separation of the two substances can be effected by recrystallisation from a mixture of benzene and ether. iso*Cholesteryl benzoate* forms small needles, m. p. 199°, $[\alpha]_D^{16}$ +73·33°. It is saponified by alcoholic potassium hydroxide, yielding iso*cholesterol*, which crystallises in long, slender needles, m. p. 140—141°. The quantity formed in the saponification agrees with the formula $C_{26}H_{45}\cdot OBz$. The molecular weight of *iso*cholesterol (in naphthalene) was found to be 372—378°, agreeing with that required by the formula $C_{26}H_{45}\cdot OH$. The substance has $[\alpha]_D^{17}$ +59·1°. In ethereal solution in presence of platinum black, it is not acted on by hydrogen. The *formate* has m. p. 108—110°; $[\alpha]_D^{17}$ +46·47°. By the action of bromine on *iso*cholesterol, a *bromo*-derivative is obtained.

R. V. S.

Nitration of Hemipinic Acid and its Esters. RUDOLF WEGSCHEIDER and ALFONS KLEMENC (*Monatsh.*, 1910, **31**, 709—743).—On energetic nitration of α-methyl hemipinate, Wegscheider and Strauch (Abstr., 1908, i, 794) obtained methyl dinitrodimethoxybenzoate, and Wegscheider and Müller (Abstr., 1908, i, 896) prepared the same compound from methyl opianate; it is therefore regarded as a derivative of 2:3-dimethoxybenzoic acid, a conclusion based on the supposition that no wandering takes place of the methyl attached to the carbonyl group during nitration. This is confirmed by the behaviour of β-methyl hemipinate, which yields a derivative of protocatechuic acid.

Hemipinic acid yields on nitration nitrohemipinic acid and small quantities of 6-nitro-2 : 3-dimethoxybenzoic acid; energetic nitration converts either of these or hemipinic acid itself directly into 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid. α-Methyl hemipinate forms the methyl ester of this acid, whereas β-methyl hemipinate forms methyl-2 : 6-dinitroveratrate. Lastly, dimethyl hemipinate forms dimethyl-5 : 6-dinitrohemipinate. In every instance on energetic nitration the esterified carboxyl group remains untouched; the unprotected carbonyl, however, is eliminated and its position occupied by a nitro-group when the second nitro-group is introduced. Apparently, methoxyl groups have a greater influence than carboxyl groups on the position occupied by the new substituting substance.

The proof of the constitution of 6-nitro-2 : 3-dimethoxybenzoic acid depends on (1) the formation from hemipinic acid, (2) the fact that it differs from the three possible nitroveratric acids, (3) the fact that it cannot be esterified by methyl alcohol and hydrogen chloride, (4) that it is convertible into 4-nitrocatechol. The constitution of 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid is established by the fact that the isomeric methyl hemipinates give isomeric dinitro-derivatives; the position 6 for one nitro-group is fixed by the formation of this acid from 6-nitro-2 : 3-dimethoxybenzoic acid, and the position 5 for the other nitro-group is established by the formation from nitrohemipinic acid.

Methyl 2 : 6-*dinitro*-3 : 4-*dimethoxybenzoate*, prepared by nitration of β-methyl hemipinate with fuming nitric acid without a solvent, crystallises in colourless, lustrous, long needles, m. p. 136—136·5°.

2 : 6-*Dinitro*iso*vanillic acid*, prepared by boiling the above compound with dilute potassium hydroxide, separates in well formed crystals, m. p. 206° (decomp.). It gives a brownish-red precipitate with ferric chloride. Crystallographic measurements prove its identity with the acid described by Matthiessen and Foster (*Jahresber.*, 1867, 520) as dinitromethylhypogallic acid. It cannot be esterified by methyl alcohol and hydrogen chloride. The *silver* salt was obtained as a yellow, crystalline, explosive substance; the *disilver* salt is red. The *methyl* ester, prepared by the interaction of methyl iodide and the mono-silver salt, crystallises in long, yellow needles, m. p. 163—164°. The *acetate* forms lustrous plates, m. p. 126—129°.

2 : 6-*Dinitroacetyl*iso*vanillic acid*, prepared by heating the acid with acetic anhydride, forms a colourless, crystalline mass, m. p. 156° (decomp.).

2 : 6-*Dinitroveratric acid*, prepared by hydrolysis of the methyl ester with the calculated amount of aqueous potassium hydroxide crystallises in long, yellow needles, which soften at 191°, m. p. 194—195°. It cannot be acetylated.

Dimethyl 6-nitrohemipinate, prepared by the action of fuming nitric acid on dimethyl hemipinate, has m. p. 83—84° [Wegscheider and Rušnov (Abstr., 1908, i, 793) found 77—78°]. It crystallises in the triclinic system, $a:b:c = 1:0·7192:0·6303$. $\alpha = 88°0'$, $\beta = 88°56'$, $\gamma = 98°31'$.

Dimethyl dinitrohemipinate crystallises in slender, colourless needles, m. p. 120—121°. On hydrolysis, *dinitrohemipinic acid*, a colourless,

crystalline powder, m. p. 163° (decomp.), is obtained. When heated in a stream of carbon dioxide at the melting point, it is converted into the *anhydride*, m. p. 113—114°.

6-Nitro-2 : 3-dimethoxybenzoic acid (Wegscheider and Rušnov, *loc. cit.*) is colourless, m. p. 189—190°, and differs from the three known nitroveratric acids. The *methyl* ester has m. p. 76—77°. By the action of aniline, 5-nitroguaiacol is formed, which yields 4-nitroveratrole on methylation.

4-*Nitroguaiacyl acetate*, prepared from nitroguaiacol and acetic anhydride, forms colourless needles, m. p. 108—109°. E. F. A.

Two Aromatic Acids of the Series, $C_nH_{2n-8}O_2$. F. BODROUX (*Bull. Soc. chim.*, 1910, [iv], 7, 847—848).—*a-Phenyl-a-ethylbutyric acid* $CEt_2Ph{\cdot}CO_2H$, obtained with the amide by the hydrolysis of the corresponding nitrile (this vol, i, 482, 557), crystallises from alcohol in small, colourless prisms, m. p. 93°. *a-Phenyl-γ-methyl-a-*iso*butylvaleric acid*, $C(CH_2Pr^{\beta})_2Ph{\cdot}CO_2H$, similarly obtained (this vol., i, 482), crystallises from light petroleum in large, colourless prisms, m. p. 75—76°. T. A. H.

Synthetic Preparation of Esters of aβ-Diphenylsuccinic Acid. TELEMACHOS KOMNENOS (*Annalen*, 1910, **375**, 254—259).—The reaction between ethereal iodine and an alcoholic solution of ethyl phenylacetate and sodium ethoxide yields ethyl (*b*)-*aβ*-diphenylsuccinate, m. p. 140°; the acid, m. p. 160°, obtained by its hydrolysis is probably a mixture of the *a* and *b* forms of *aβ*-diphenylsuccinic acid. Ethereal iodine reacts with a methyl-alcoholic solution of ethyl phenylacetate and sodium methoxide to form *methyl* (*a*)-*aβ-diphenylsuccinate*,

$$[CO_2Me{\cdot}CHPh]_2,$$

m. p. 210°; the acid obtained by its hydrolysis softens at 187°, melts at 222° (decomp.), and forms a barium salt containing $2H_2O$, and is, therefore, (*a*)-*aβ*-diphenylsuccinic acid. C. S.

Action of Unsaturated Dicarboxylic Acids on *p*-Aminophenols. ARNALDO PIUTTI (*Gazzetta*, 1910, **40**, i, 525—568. Compare Abstr., 1908, i, 783; this vol., i, 22, 264).—[With A. PAGNIELLO and A. MARCIANO.]—*Citraconic Derivatives.*—p-*Hydroxyphenylcitraconamic acid*, $C_{11}H_{11}O_4N$, forms yellow, acicular prisms, m. p. 155°. p-*Methoxyphenylcitraconamic acid*, $C_{12}H_{13}O_4N$, may be obtained by the method previously given, and also (1) by saponifying *p*-methoxyphenylcitraconimide with alcoholic potassium hydroxide; (2) by acting on *p*-anisidine (in light petroleum) with mesaconyl chloride. It crystallises in long, yellow prisms, m. p. 167°, and gives a violet coloration with ferric chloride. p-*Ethoxyphenylcitraconamic acid*, $C_{13}H_{15}O_4N$, prepared by the above methods, forms yellow needles, m. p. 162°, and gives a yellow coloration with ferric chloride.

p-*Hydroxyphenylcitraconimide*, $C_{11}H_9O_3N$, is a dark yellow, crystalline substance, m. p. 170°. p-*Methoxyphenylcitraconimide*, $C_{12}H_{11}O_3N$, forms yellow crystals, m. p. 121°; it gives a violet coloration with alcoholic potassium hydroxide. p-*Ethoxyphenylcitraconimide*,

$$C_{13}H_{13}O_3N,$$

crystallises in canary-yellow needles, m. p. 109°.

The diamides obtained from citraconic anhydride or citraconyl chloride by the methods already indicated are found to be mesaconic derivatives, identical with those obtained directly from mesaconic acid. The *p*-hydroxyphenyl derivative could not be obtained. p-*Methoxyphenylmesacondiamide*, $C_{19}H_{20}O_4N_2$, forms colourless, lustrous scales, m. p. 206°. p-*Ethoxyphenylmesacondiamide*, $C_{21}H_{24}O_4N_2$, crystallises similarly, and has m. p. 205°.

[With C. SCHIFANI.]—*Mesaconic Derivatives.*—Mesaconamic acids and mesaconimides could not be prepared, but in their stead corresponding citraconic derivatives appeared. On the other hand, *p*-methoxy- and *p*-ethoxy-phenylmesacondiamides were obtained, identical with those from citraconic acid (*v.s.*).

By the action of mesaconyl chloride on *p*-anisidine in addition to *p*-methoxyphenylcitraconamic acid, a colourless *substance*, m. p. 235°, was obtained.

[With IDA FOA and L. ROSSI.]—*Itaconic Derivatives.*—Of the four isomeric p-*hydroxyphenylitaconamic acids*, $C_{11}H_{11}ON_4$, which might be expected, only three could be prepared. On mixing equimolecular quantities of itaconic anhydride and *p*-aminophenol, dissolved in benzene and in acetone respectively, one isomeride is precipitated; it forms colourless needles, m. p. 161—162° (forming a yellowish-brown liquid), and gives no coloration with ferric chloride. The *silver* salt was prepared. Another isomeride, a yellow, crystalline powder, m. p. 118—119°, is obtained by dissolving the corresponding imide in sodium hydroxide and precipitating with acid; it gives a red coloration with ferric chloride. When it is boiled with water, it yields the third isomeride, which is colourless, has m. p. 97—98°, and gives no coloration with ferric chloride. By similar methods, three corresponding isomeric p-*methoxyphenylitaconamic acids*, $C_{12}H_{13}O_4N$, are obtained. The first forms colourless, acicular crystals, m. p. 166—167° (forming a yellow liquid), and gives no coloration with ferric chloride. The *silver* salt was obtained. The second isomeride is yellow, and has m. p. 144—145°; it yields a red coloration with ferric chloride. The *silver* salt was prepared. The other isomeride is colourless, has m. p. 135—136°, and gives no coloration with ferric chloride. The *silver* salt was prepared. There are three corresponding isomeric p-*ethoxyphenylitaconamic acids*, $C_{13}H_{15}O_4N$. The first forms colourless, lustrous scales, m. p. 165—166°, and gives no reaction with ferric chloride. The *silver* salt was prepared. A second isomeride forms a yellow precipitate, m. p. 148—149°, and gives a red coloration with ferric chloride. The *silver* salt was prepared. The third isomeride is a colourless, crystalline substance, m. p. 134—135°. The *silver* salt was also obtained.

The imides corresponding with the above acids were prepared (1) by heating the acids in an atmosphere of carbon dioxide at a temperature a little above their melting points; (2) by heating at 130° in carbon dioxide mixtures of itaconic anhydride with the aminophenols. p-*Hydroxyphenylitaconimide*, $C_{11}H_9O_3N$, forms yellow crystals, m. p. 104—105°. p-*Methoxyphenylitaconimide*, $C_{12}H_{11}O_3N$, crystallises in small, yellow needles, m. p. 101—102°; it gives an intense, reddish-violet coloration with sodium ethoxide. p-*Ethoxyphenylitaconimide*,

$C_{13}H_{13}O_3N$, forms yellow needles, m. p. 99—100°, and gives a reddish-violet coloration with potassium or sodium hydroxide.

The itacondiamides were obtained by the method previously described. p-*Hydroxyphenylitacondiamide*, $C_{17}H_{16}O_4N_2$, crystallises in small, light brown laminæ, m. p. 132—133°. p-*Methoxyphenylitacondiamide*, $C_{19}H_{20}O_4N_2$, forms lustrous scales, m. p. 155—156° p-*Ethoxyphenylitacondiamide*, $C_{21}H_{24}O_4N_2$, crystallises similarly, and has m. p. 173—174°.

[With GINO ABATI.]—*Pyrocinchonic Derivatives.*—Of the derivatives of this acid, only the imides could be prepared, in addition to *p*-anisidine *p*-methoxyphenylpyrocinchonamate,

$$C_2Me_2(CO{\cdot}NH{\cdot}C_6H_4OR)_2,$$

and *p*-phenetidine *p*-ethoxyphenylpyrocinchonamate.

p-*Hydroxyphenylpyrocinchonimide*, $C_{12}H_{11}O_3N$, was obtained by (1) heating to boiling point an alcoholic solution of pyrocinchonic anhydride and *p*-aminophenol, a current of sulphur dioxide being afterwards passed to reduce the coloration of the liquid; (2) mixing the two substances in the presence of acetone in the cold, sulphur dioxide being afterwards employed to decolorise the liquid. In the latter case, indications were obtained of the formation and subsequent decomposition of *p*-aminophenol *p*-hydroxyphenylpyrocinchonamate. When the imide is treated with alcoholic potassium hydroxide and then acidified, it separates out unchanged. The imide forms large, canary-yellow crystals, m. p. 200°. When it is precipitated from alcohol with water, or when it is powdered in a mortar, it is obtained in colourless crystals, which have the same m. p. and composition as the other form.

p-Anisidine and pyrocinchonic anhydride in alcoholic solution in the warm, and in acetone at the ordinary temperature, yield p-*methoxyphenylpyrocinchonimide*, $C_{13}H_{13}O_3N$, crystallising in straw-yellow prisms, m. p. 139°. From some solvents it is obtained in colourless crystals, which become yellow on melting, and remain so on resolidification. *p*-Anisidine and the anhydride react in benzene solution at the ordinary temperature, yielding p-*anisidine* p-*methoxyphenylpyrocinchonamate*, $C_{20}H_{24}O_5N_2$, which forms small, white needles, m. p. 90—91° (becoming yellow at about 85°). In solution (in ethylene bromide) the substance decomposes into its three constituents. p-*Ethoxyphenylpyrocinchonimide*, $C_{14}H_{15}O_3N$, forms lustrous, yellow needles, m. p. 117°. The colourless form has m. p. 116—117°. p-*Phenetidine* p-*ethoxyphenylpyrocinchonamate* crystallises in minute, colourless needles, which become yellow at 80° and melt at 94° to a yellow liquid, which remains yellow on solidification.

[With C. ALLEGRI.]—*Phthalic, Citraconic, Itaconic, and Maleic Derivatives of* o-*Anisidine.*—o-*Methoxyphenylphthalamic acid*,

$$C_{15}H_{13}O_4N,$$

forms colourless crystals, m. p. 168—169°, and gives with ferric chloride a yellow coloration, which becomes reddish-violet. o-*Methoxyphenylcitraconamic acid*, $C_{12}H_{13}O_4N$, crystallises in canary-yellow needles, m. p. 116—117°, and yields an intense reddish-violet coloration with ferric chloride. o-*Methoxyphenylitaconamic acid*, $C_{12}H_3O_4N$, forms small, colourless needles, m. p. 128—129°, and gives a pale

violet coloration with ferric chloride. o-*Methoxyphenylmaleinamic acid*, $C_{11}H_{11}O_4N$, an amorphous, yellow powder, has m. p. 144—145°, and gives with ferric chloride a wine-red coloration.

o-*Methoxyphenylphthalimide*, $C_{15}H_{11}O_3N$, crystallises in colourless prisms, m. p. 155—156°. o-*Methoxyphenylcitraconimide*, $C_{12}H_{11}O_3N$, a pale yellow powder, has m. p. 98—99°, and gives a violet coloration with alcoholic potassium hydroxide. o-*Methoxyphenylitaconimide*,

$$C_{12}H_{11}O_3N,$$

is a colourless powder, m. p. 112—113°. *o*-Methoxyphenylmaleinimide could not be obtained.

[With G. LEONE and C. D'EMILIO.]—*Camphoric Derivatives.*—α-cis-p-*Hydroxyphenylcamphoramic acid*, $\overset{H}{\underset{Me}{}}\!>\!C_7H_{10}\!<\!\overset{CO\cdot NH\cdot C_6H_4\cdot OH}{\underset{CO_2H}{}}$, prepared by heating camphoric anhydride and *p*-aminophenol in boiling acetone for half an hour, has m. p. 165° (becoming brown at 155°), $[\alpha]_D^{16}$ $+46{\cdot}36°$. α-trans-p-*Hydroxyphenylcamphoramic acid*, $\overset{H}{\underset{CO_2H}{}}\!>\!C_7H_{10}\!<\!\overset{CO\cdot NH\cdot C_6H_4\cdot OH}{\underset{Me}{}}$, is obtained when an aqueous solution of the potassium salt of the preceding acid is heated for ten hours in an autoclave at 120°, and then treated with hydrochloric acid; it has m. p. 226°, $[\alpha]_D^{16}$ $+13{\cdot}48°$. α-p-*Hydroxyphenylcamphoramic acid* (?), $C_{16}H_{21}O_4N$, from camphoric anhydride and *p*-aminophenol in acetone at the ordinary temperature, becomes brown at 205° and decomposes at 220°, and has $[\alpha]_D^{16}$ $+52{\cdot}4°$. When heated in alcoholic solution, it is converted into the α-*cis*-form, m. p. 165°. A p-*hydroxyphenylcamphoramic acid* (?), $C_{16}H_{21}O_4N$, is also obtained by heating camphoric anhydride and *p*-aminophenol in a sealed tube for five hours at 210°. It forms colourless crystals, m. p. 185°, $[\alpha]_D^{16}$ $+12{\cdot}4°$. A p-*methoxyphenylcamphoramic acid* (?), $C_{17}H_{23}O_4N$, is obtained on mixing benzene solutions of camphoric anhydride and *p*-anisidine. It forms large, colourless prisms, m. p. 198°. α-cis-p-*Ethoxyphenylcamphoramic acid*, $C_{18}H_{25}O_4N$, is prepared by heating camphoric anhydride with *p*-phenetidine for two hours, or by heating without a solvent for eight hours in an autoclave. It forms colourless crystals, m. p. 199°, $[\alpha]_D^{16}$ $+51{\cdot}4°$. α-trans-p-*Ethoxyphenylcamphoramic acid* is obtained in the same way as the corresponding methoxy-derivative. It has m. p. 184°, $[\alpha]_D^{25}$ $+2{\cdot}81°$.

p-*Hydroxyphenylcamphorimide*, $C_{16}H_{19}O_4N$ (from camphoryl chloride and *p*-aminophenol in acetone), has m. p. 218°, $[\alpha]_D^{25}$ $+5{\cdot}49°$. p-*Methoxyphenylcamphorimide*, $C_{17}H_{21}O_3N$, forms colourless crystals, m. p. 110°. p-*Ethoxyphenylcamphorimide* crystallises in colourless needles, m. p. 114°, $[\alpha]_D^{25}$ $-13{\cdot}28°$.

[With D. PUGLIESE and G. SELVAGGI.]—iso*Phthalic and Terephthalic Derivatives.*—No product of the action of *iso*phthalic acid on *p*-aminophenol in boiling alcohol could be isolated. The reactions with *p*-anisidine and *p*-phenetidine respectively, under the same conditions, yielded p-*anisidine hydrogen phthalate*, which on heating becomes brown above 200°, and p-*phenetidine hydrogen phthalate*, which becomes brown on heating above 100°. p-*Methoxyphenyl*iso*phthaldiamide*,

$$C_6H_4(CO\cdot NH\cdot C_6H_4\cdot OMe)_2,$$

was obtained, however, by heating the acid with *p*-anisidine to 280°.

It crystallises in colourless needles, m. p. 268°. p-*Methoxyphenylterephthaldiamide*, similarly obtained by heating to 150°, forms lustrous scales, m. p. 246—248°. p-*Ethoxyphenylterephthaldiamide*, similarly prepared by heating at 180° for two hours, forms grey needles, which, on heating to 300°, become brown, but do not melt. R. V. S.

Galloflavin. VI. Lactone Dyes. JOSEF HERZIG [with GEZA ERDÖS and GRETE RUZICKA] (*Monatsh.*, 1910, **31**, 799—818. Compare Herzig and Epstein, Abstr., 1908, i, 899).—Galloflavin belongs to quite a different class of substances than resoflavin, which is classed as a derivative of diphenylbimethylolide. Galloflavin is completely methylated by diazomethane (Herzig and Tscherne, Abstr., 1904, i, 814). Unlike resoflavin, on further treatment of this methylated derivative with potassium hydroxide and methyl sulphate or methyl iodide, it cannot be converted into the methyl ethyl ester, but yields a mixture of tarry products. A further point of difference is in the behaviour towards potassium hydroxide; methyl galloflavin dissolved in the cold yields on acidification a hydrolysed substance with fewer methoxyl groups, and the latter when methylated gives a substance isomeric with the original. The new compound is provisionally termed iso*galloflavin trimethyl ether*, $C_{12}H_3O_5(OMe)_3$, and the new ether is iso*galloflavin tetramethyl ether*, $C_{12}H_2O_4(OMe)_4$. Galloflavin, therefore, has the formula $C_{12}H_2O_4(OH)_4$, with which the analysis of the acetyl derivative agrees.

The conversion into *iso*galloflavin trimethyl ether gives only about 45% of the theoretical yield, together with a syrupy product.

*iso*Galloflavin trimethyl ether is a pronounced acid; at the melting point carbon dioxide is eliminated, forming the *compound*,

$$C_{11}H_3O_3(OMe)_3.$$

It contains a lactone ring which is opened by treatment with potassium hydroxide and methyl iodide or sulphate, yielding a crystalline substance. This *ether* ester is quantitatively hydrolysed to the *ether acid*, $C_{10}H_2O(OMe)_4(CO_2H)_2$, which again loses carbon dioxide at the melting point, forming an acid, $C_{10}H_3O(OMe)_4 \cdot CO_2H$. It remains to determine the function of the last oxygen atom, the constitution of the complex, $C_{10}H_8$ or $C_{10}H_{10}$, and the relation of the *iso*-derivative to galloflavin.

Purpurogallin, $C_{11}H_4O(OH)_4$, has been shown by A. G. Perkin to undergo an isomerisation with potassium hydroxide similar to galloflavin, and it is possible that the C_{10} complex is the same in each case.

Tetra-acetylgalloflavin is colourless, m. p. 230—233°. Galloflavin tetramethyl ether forms colourless, matted needles, m. p. 236—239°. iso*Galloflavin trimethyl ether* forms colourless needles, m. p. 253—256° (decomp.). iso*Galloflavin tetramethyl ether* crystallises in well-formed, long needles, m. p. 232—234°, mixed m. p. with the isomeride 205—211°.

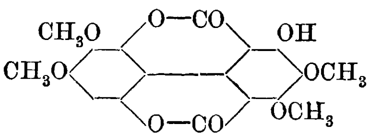
The *compound*, $C_{11}H_3O_3(OMe)_3$, formed on heating *iso*galloflavin trimethyl ether, separates from alcohol in colourless crystals, m. p. 130—134°.

The *ether* ester, $C_{12}H_2O_3(OMe)_6$, has m. p. 93—95°; the *ether acid*, $C_{12}H_4O_5(OMe)_4$, is colourless; it becomes coloured at 205°, m. p.

214—215° (decomp.). Heated at 210—220°, carbon dioxide is eliminated, and the *compound*, $C_{11}H_4O_3(OMe)_4$, m. p. 132—134°, is obtained.

Acetylpurpurogallin forms colourless plates, m. p. 181—183°. Tetramethylpurpurogallin is colourless, m. p. 91—92° (compare Perkin, Proc., 1905, **21**, 211). E. F. A.

Condensation Products of Gallic Acid Di- and Tri-methyl Ether. VII. Lactone Dyes. JOSEF HERZIG and F. SCHMIDINGER (*Monatsh.*, 1910, **31**, 819—826).—By the condensation of either gallic acid 3:4-dimethyl ether or gallic acid trimethyl ether by means of potassium persulphate, *flavellagic acid tetramethyl ether* (annexed formula), a yellow dye, is obtained.



When purified through the *acetyl* derivative, m. p. 237—238°, it crystallises in minute, sulphur-yellow needles, m. p. 270—271°.

By the action of potassium hydroxide and methyl sulphate, the lactone ring is opened, and flavellagic acid methyl ether ester (the completely methylated product), m. p. 81°, is obtained (compare Herzig and Tscherne, Abstr., 1908, i, 547). Diazomethane is entirely without action on the condensation product, although this readily converts flavellagic acid into the pentamethyl derivative. Apparently the resistant hydroxyl is rendered so by the presence of the methoxyl groups, and the same group is methylated at an early stage in the case of flavellagic acid itself. E. F. A.

Synthesis of Glucosyringic Acid. FERDINAND MAUTHNER (*J. pr. Chem.*, 1910, [ii], **82**, 271—274).—*Methyl tetra-acetylglucosyringate*, $C_{24}H_{30}O_{14}$, m. p. 106—107°, obtained by shaking a solution of methyl syringate in aqueous sodium hydroxide with ethereal β-acetobromoglucose for twenty-four hours, is hydrolysed by 6% barium hydroxide, whereby is obtained glucosyringic acid identical with that produced by the oxidation of syringin. C. S.

Degradation of *cyclo*Gallipharic Acid by Oxidising Agents. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Arch. Pharm.*, 1910, **248**, 398—420).—When *cyclo*gallipharic acid, hydrolysed by sodium hydroxide, is heated for twelve hours on the water-bath with the gradual addition of 3·5% hydrogen peroxide, carbon dioxide and acraldehyde are evolved, and, after acidification, a colourless, crystalline monobasic *acid*, $C_{18}H_{34}O_3$, m. p. 76°, is obtained, which develops a bluish-violet coloration with alcoholic ferric chloride. This reaction suggests that the acid is still a cyclic compound containing hydroxyl and carboxyl groups in the ortho-position; the acid is an oxidation product intermediate between *cyclo*gallipharic acid and gallipharic acid, and consequently is called cyclomeso*gallipharic acid*. When *cyclo*gallipharic acid and an excess of sodium hydroxide on the water-bath are treated with 3·5% hydrogen peroxide until the bluish-violet coloration is no longer produced with ferric chloride, the products of

oxidation are found to be acraldehyde, butyric acid, and gallipharic acid, m. p. 57·5° (not 54°).

The oxidation of *cyclo*gallipharic acid by sodium carbonate and 3% potassium permanganate has been shown to produce butyric and oxalic acids, glycerol, and gallipharic acid, m. p. 54° (Kunz-Krause and Schelle, Abstr., 1904, i, 587). The gallipharic acid is now shown, by analyses of the acid and of the sodium and silver salts, to be a mixture of about 75% gallipharic acid, m. p. 57·5°, and 25% of *gallipinic acid*, $C_{14}H_{28}O_2$, m. p. 49°, which is separable by dilute alcohol. In addition to these two, a small quantity of a third acid, *polycyclopharic acid*, $C_{30}H_{60}O_5$, m. p. 35°, has been isolated, which gives a Bordeaux-red coloration with ferric chloride, and develops in the liquid state an olive-green fluorescence and a pronounced odour of oranges. The greater part of these acids is absorbed by the hydrated manganese dioxide produced during the oxidation, and is extracted therefrom, after drying, by alcohol. The residue is freed from manganese dioxide by hot concentrated oxalic acid, and the residual yellow mass is purified by repeated solution in acetone and evaporation of the solvent, whereby a reddish-brown resin, *resocyclopharol*, $C_{15}H_{24}O_3$, m. p. 93°, is obtained, which has a pleasant odour of oranges, and in solution an acid reaction and olive-green fluorescence.

The oxidation of *cyclo*gallipharic acid by alkaline potassium permanganate yields 28·10% of gallipinic and gallipharic acids, 44·96% of resocyclopharol, 16·20% of oxalic acid, 1·64% of butyric acid, and 2·20% of glycerol. C. S.

Anthraquinone-2 : 3-dicarboxylic Anhydride. CONRAD WILLGERODT and FRANCESCO MAFFEZZOLI (*J. pr. Chem.*, 1910, [ii], 82, 205—231).—The following results are the outcome of an unsuccessful attempt to obtain an anthraquinone-indigotin from anthraquinone-2 : 3-dicarboxylic anhydride by a method analogous to Heumann's synthesis.

Anthraquinone-2 : 3-dicarboxylic anhydride, which is precipitated almost quantitatively when the acid is boiled with acetic anhydride for fifteen minutes, is best converted into the imide by heating its intimate mixture with ammonium thiocyanate at 160—170° for five minutes, or with carbamide at 175—180° for one hour. *Anthraquinone-3-carbonamide-2-carboxylic acid*, $C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2(CO\cdot NH_2)\cdot CO_2H$, m. p. above 340°, prepared by dissolving the imide in dilute alkali at 40—50°, is converted into *3-aminoanthraquinone-2-carboxylic acid*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2(NH_2)\cdot CO_2H,$$

by oxidising its alkaline solution with freshly prepared sodium hypobromite, or, better, with 5·4% sodium hypochlorite, at 80—85°, or, quantitatively, with iodosobenzene; in all three cases a blood-red, crystalline alkali salt is precipitated, from which the amino-acid is liberated by hydrochloric acid and recrystallised from nitrobenzene; it then separates in orange-yellow needles. The amino-acid, the *ammonium*, *sodium*, *silver*, and *barium* salts of which are described, does not yield salts with acids, forms a yellow *acetyl*

derivative, m. p. 248°, yields 2-aminoanthraquinone by the heating of its silver salt, and is converted into anthraquinone-2-carboxylic acid when the amino-group is replaced by hydrogen in the usual way. When heated with chloroacetic acid for half an hour, it yields, not the desired glycine derivative, but *3-chloroacetylaminoanthraquinone-2-carboxylic acid*, $C_6H_4<\substack{CO\\CO}>C_6H_2(CO_2H)\cdot NH\cdot CO\cdot CH_2Cl$, m. p. 350°, which forms microscopic, orange crystals. When a pyridine solution of the imide mentioned above is diluted with an equal volume of alcohol and treated with alcoholic potassium hydroxide, the *potassium* derivative, $C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{CO\\CO}>NK$, is obtained as a brownish-grey powder, which is converted by water at 40—50° into potassium anthraquinone-3-carbonamide-2-carboxylate, and reacts with ethyl chloroacetate at 150—160° to form the *ester*,

$$C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{CO\\CO}>N\cdot CH_2\cdot CO_2Et,$$

m. p. 241—242°. When treated with the calculated quantity of sodium hydroxide solution at 40—50°, this ester yields the *compound*, $C_6H_4<\substack{CO\\CO}>C_6H_2(CO_2H)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 313—314°, an alkaline solution of which is converted by sodium hypochlorite into anthraquinone-2-carboxylic acid, anthraquinone-2 : 3-dicarboxylic acid, and 3-aminoanthraquinone-2-carboxylic acid.

Anthraquinonefluorescein,

$$C_6H_4<\substack{CO\\CO}>C_6H_2\overset{CO\cdot O}{\diagup\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\diagdown}C<\substack{C_6H_3(OH)\\C_6H_3(OH)}>O,$$

which is obtained by adding zinc chloride to an intimate mixture of resorcinol and anthraquinone-2 : 3-dicarboxylic anhydride at 150° and heating the mass at 180—190° for five to six hours (the purification of the product is troublesome), crystallises in yellow needles, m. p. above 380°. It forms in concentrated alkali a dark cherry-red, non-fluorescent solution, which becomes reddish-yellow by dilution and then exhibits a very feeble red fluorescence. The *ammonium, silver, barium, calcium, magnesium,* and *lead* salts of the fluorescein, which possesses feeble acid properties, are described. The *diacetyl* derivative, m. p. 259—260°, is hydrolysed by boiling alcoholic alkalis or by cold concentrated sulphuric acid, but not by boiling concentrated hydrochloric acid. When the powdered fluorescein is exposed in a desiccator to bromine vapour for three to four hours, it is converted into a red *dibromoanthraquinonefluorescein*, $C_{28}H_{12}O_7Br_2$, m. p. 313° (decomp.), which is soluble in alkalis and forms highly coloured salts. *Tetrabromoanthraquinonefluorescein*, $C_{28}H_{10}O_7Br_4$, m. p. 367° (decomp.), is obtained by adding the calculated amount of bromine to a cold alcoholic solution of anthraquinonefluorescein and precipitating the substance by water. The alkali salts of this and of the dibromo-derivative are dyes which have a great affinity for animal fibres.

Anthraquinone-2 : 3-dicarboxylic anhydride, quinaldine, and zinc chloride react at 180—190° to form a *substance*,

$$C_6H_4<\substack{CO\\CO}>C_6H_2\overset{CO\cdot O}{\diagup\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\diagdown}C{:}CH\cdot C_9NH_6,$$

which crystallises in microscopic, yellow needles, does not melt below 380°, and dissolves unchanged in concentrated sulphuric acid.

C. S.

Piperonylidene Diacetate. JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 713—715).—Acetic anhydride in the presence of a drop of sulphuric acid converted piperonal into *piperonylidene diacetate*, which separated from alcohol in colourless, transparent crystals, m. p. 51°. After a time these crystals became opaque, their m. p. having changed to 80°. Various attempts to obtain again the modification with m. p. 51° were made, but proved unsuccessful. A. J. W.

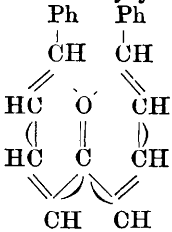
Synthesis of a New Gallacetophenone Trimethyl Ether. FERDINAND MAUTHNER (*J. pr. Chem.*, 1910, [ii], 275—280).—3 : 4 : 5-*Trimethoxyphenyl methyl ketone*, $CH_3 \cdot CO \cdot C_6H_2(OMe)_3$, m. p. 72°, is obtained by the action for fourteen days of ethereal diazomethane on a benzene solution of gallaldehyde trimethyl ether. A more convenient process starts from ethyl 3 : 4 : 5-trimethoxybenzoylacetate (best prepared by the condensation of ethyl acetate and methyl gallate trimethyl ether under the influence of sodium), which is converted into the ketone by heating for nine hours with 25% sulphuric acid. The p-*nitrophenylhydrazone*, m. p. 195—196°, separates from hot alcohol in reddish-brown needles; the *semicarbazone* has m. p. 178—179°.

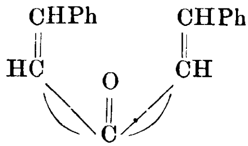
C. S.

Distribution of Affinity in Unsaturated Organic Compounds. WALTHER BORSCHE (*Annalen*, 1910, 375, 145—180).—In a conjugated system of two unsaturated groups, the residual affinities of the inner pair of unsaturated atoms neutralise each other, leaving free residual affinity only at the two external unsaturated atoms, where addition takes place. Thiele's conception, thus stated, is incorrect, for the inner pair of atoms still retain the power of increasing the mobility of univalent atoms attached to them through the intermediary of saturated multivalent atoms, and therefore still retain residual affinity. (According to Thiele, the increased mobility of a univalent atom, exhibited when the atom is attached to an unsaturated group through the intermediary of a saturated multivalent atom, as, for example, $\underset{\dot{O}H}{\cdots C{:}O\cdots}$, is caused by the influence of the residual affinity of the unsaturated carbon atom on the hydroxylic oxygen atom, whereby the hold of the latter on the hydrogen is weakened.) The affinity (strictly speaking, that portion of the affinity which denotes the unsaturation) of an unsaturated atom in a conjugated system, therefore, is divided into three parts; for example, in the system, $\underset{\alpha}{C}{:}\underset{\beta}{C}\cdot\underset{\gamma}{C}{:}\underset{\delta}{C}$, the affinity of C_β is divided into (i) the portion denoted in the double linking, (ii) the portion which is neutralised by the corresponding portion of the affinity of C_γ, (iii) the portion which persists as free residual affinity. At present little can be stated with regard to the quantitative proportions of these three parts; most probably they are different in each individual case. The distribution of the affinity in a conjugated system of

two unsaturated groups is such that there is a tendency for the neutralisation of the residual affinities of the inner pair of unsaturated atoms, and for the accumulation of residual affinity at the outer pair.

The distribution of the affinity in a conjugated system of three unsaturated groups forming a straight chain is very similar to the preceding, but the accumulation of residual affinity at the outer unsaturated atoms does not necessarily indicate great additive capacity, because in a chain of six atoms the last is near enough to the first for their residual affinities to more or less neutralise one another; for example, under suitable conditions, ethyl acetoacetate forms an additive compound with distyryl ketone, but not with dicinnamylideneacetone :





In conjugated systems containing "crossed" doubling linkings, $\underset{\text{---O---}}{\overset{}{\text{C:C·C·C:C}}}$, there are three outer atoms at which the residual affinity can collect, and therefore the distribution of the affinity is more complicated. In the simple system $\underset{\text{O--}}{\text{C:C·C}}$, the affinity of the carbonyl carbon atom neutralises more or less that of the adjacent carbon atom ; in the "crossed" system the central carbon atom, in order to neutralise the affinities of each of the adjacent carbon atoms, utilises more of its affinity ; consequently, the oxygen atom has a greater amount of free residual affinity. There is more residual affinity at the three outer unsaturated atoms in a conjugated system of crossed double linkings than at the ends of a chain of three unsaturated groups forming a conjugated system; in the former system the neutralisation of the affinities of the three inner unsaturated atoms is less complete, the state of equilibrium first attained is more labile, and the system is more prone to enter into reaction. Such reactions will occur preferentially at the oxygen atom (or other multivalent atom attached to the central carbon atom), the more so as the unsaturated atoms at the other two ends of the crossed system are so situated as to neutralise each other's residual affinity more or less completely.

The views developed above have been tested by experiments on the addition of ethyl acetoacetate and other compounds containing activated methylene groups to $\alpha\beta$-unsaturated ketones of the type of distyryl ketone, therefore, to substances containing the conjugated system of crossed double linkings, $\underset{\text{O}}{\text{C:C·C·C:C}}$.

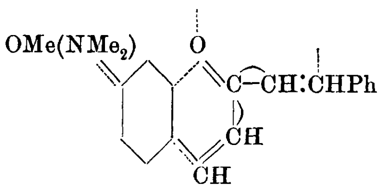
According to the old view, a carbonyl group increases the additive power of a contiguous ethylenic linking without itself playing an active part in the addition. Consequently, there should be less tendency for the addition of a molecule, XY, to substances containing such a system than to substances containing the group $\underset{\overset{\cdot\cdot}{O}}{C{:}C{\cdot}C{\cdot}}$, because in the former case the activating influence of the carbonyl group is diffused over two ethylenic linkings. When, however, one molecule of XY has been attached, the resulting system, CX·CY·CO·C:C, will have a greater additive power than the original system; consequently, the final product should be CX·CY·CO·CY·CX. According to the author's views, the system C:C·CO·C:C has a greater additive power than C:C·CO·C, and the final product will be CX·CY·CO·C:C. Now Knoevenagel and Speyer (Abstr., 1902, i, 226) have shown that equal molecular quantities of distyryl ketone and ethyl acetoacetate yield a substance, $C_{23}H_{24}O_4$, which they formulate as $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Et){\cdot}COMe$. Rabe and Elze (Abstr., 1902, i, 709) have shown that the substance has the constitution $CHPh{:}CH{\cdot}C(OH){<}\begin{matrix}CH_2{\cdot}CHPh\\CH_2{-\!-\!-}CO\end{matrix}{>}CH{\cdot}CO_2Et$.

This constitution, which is confirmed by the author, is not a proof of the author's views, because even by the older theory the substance should be incapable of adding on a second molecule of ethyl acetoacetate, since it does not contain a carbonyl group in the immediate neighbourhood of the ethylenic linking. Similar cyclic β-ketone alcohols have been obtained from distyryl ketone and acetylacetone or benzoylacetone (the three β-ketone alcohols very easily lose a molecule of water, probably because the residual affinity of the nearer carbon atom in the ethylenic group renders the hydroxyl group more mobile by neutralising some of the affinity of the carbon atom to which it is attached). The author's view, however, is fully supported by the behaviour of ethyl benzoylacetate or ethyl malonate, which, even in excess, reacts with distyryl ketone to form the compounds

$$CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Et){\cdot}COPh$$

and $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Et)_2$. Dianisylideneacetone, tetramethyl-*pp'*-diaminodibenzylideneacetone, and dicinnamylideneacetone do not react with ethyl acetoacetate under the conditions in which distyryl ketone reacts so easily; benzylideneanisylideneacetone-*p*-dimethylaminodistyryl ketone, and benzylidenecinnamylideneacetone do combine with 1 mol. of ethyl acetoacetate, but less readily than distyryl ketone. It follows from these six examples that the groups $OMe{\cdot}C_6H_4{\cdot}$, $NMe_2{\cdot}C_6H_4{\cdot}$, and CHPh:CH· must in some way diminish the residual affinity, not only of the two external unsaturated carbon atoms, $\underset{\overset{\cdot\cdot}{O}}{C{:}\overset{\frown}{C}{\cdot}\overset{\frown}{C}{\cdot}C{:}C}$, but also of the carbonyl oxygen atom, the residual affinity of which influences the additive power of the two ethylenic linkings. The explanation in the case of dicinnamylideneacetone has been given above; in the cases of benzylideneanisylidene-

acetone and *p*-dimethylaminodistyryl ketone, the author suggests a distribution of the affinity represented in the annexed formula.



The following compounds are described: Ethyl 3-phenyl-5-styryl*cyclo*hexan-5-ol-1-one-2-carboxylate, prepared by Knoevenagel and Speyer (*loc. cit.*), is also obtained quantitatively when a mixture of distyryl ketone, ethyl acetoacetate, and a little piperidine is heated on the water-bath for a few hours and is then kept at the ordinary temperature. It is best converted into ethyl 3-phenyl-5-styryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate by heating its alcoholic solution with sodium ethoxide or piperidine. The *cyclo*hexene derivative yields a *benzyl* derivative, m. p. 128—129°, is converted by boiling glacial acetic and 20% sulphuric acids into 3-*phenyl*-5-*styryl*-Δ^5-cyclo*hexenone*, m. p. 110—111°, and by prolonged treatment with alcoholic sodium ethoxide is changed into an *isomeride*, m. p. 159°, of unknown constitution. *Ethyl α-benzoyl-γ-cinnamoyl-β-phenylbutyrate*, $CHPh{:}CH\cdot CO\cdot CH_2\cdot CHPh\cdot CHBz\cdot CO_2Et$, m. p. 134°, obtained quantitatively by keeping a mixture of distyryl ketone, ethyl benzoylacetate, and a little piperidine in ether for many days, forms a *dibromide*, m. p. 180°, and is decomposed into its generators by heating with 10% sodium hydroxide. Distyryl ketone, acetylacetone, and a little piperidine yield 2-*acetyl*-3-*phenyl*-5-*styryl*cyclo*hexan*-5-*ol*-1-*one*, $CHPh{:}CH\cdot C(OH){<}\begin{matrix}CH_2\cdot CHPh\\ CH_2 —— CO\end{matrix}{>}CHAc$, m. p. 134—135°; a by-product of the reaction is 2-*acetyl*-3-*phenyl*-5 *styryl*-Δ^5-cyclo*hexenone*, m. p. 157—158°, which becomes the main product when the mixture is heated with alcohol for two to three days. 2-*Benzoyl*-3-*phenyl*-5-*styryl*-cyclo*hexan*-5-*ol*-1-*one*, m. p. 130°, and 2-*benzoyl*-3-*phenyl*-5-*styryl*-Δ^5-cyclo*hexenone*, m. p. 171°, are obtained when a mixture of distyryl ketone, benzoylacetone, and a little piperidine in alcohol is heated for two hours and for one day respectively. *Ethyl γ-cinnamoyl-β-phenyl-propane-αα-dicarboxylate*, $CHPh{:}CH\cdot CO\cdot CH_2\cdot CHPh\cdot CH(CO_2Et)_2$, m. p. 79°, obtained by heating a mixture of distyryl ketone, ethyl malonate, alcohol, and a little piperidine for two days on the water-bath, forms a *phenylcarbamic acid hydrazone*, m. p. 171°, and in alcoholic solution is hydrolysed by 25% sodium hydroxide at the ordinary temperature, yielding ultimately the free *acid*, m. p. 147—148° (decomp.), which is converted by heating into *γ cinnamoyl-β-phenylpropionic acid*,

$$CHPh{:}CH\cdot CO\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO_2H,$$

m. p. 158—159°.

Benzylideneanisylideneacetone, ethyl acetoacetate, and a little piperidine yield *ethyl* 3-*phenyl*-5-p-*methoxystyryl*cyclo*hexan*-5-*ol*-1-*one*-2-*carboxylate*, m. p. 142°, which loses H_2O when heated with 10% sodium hydroxide, *ethyl* 3-*phenyl*-5-p-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carb oxylate*, m. p. 135°, being formed. p-*Dimethylaminodistyryl ketone*, m. p. 158°, which is best prepared by keeping a mixture of styryl methyl ketone, *p*-dimethylaminobenzaldehyde, and 10% sodium hydr-

oxide in 50% alcohol for a few weeks, reacts extremely slowly with ethyl acetoacetate in the presence of a little piperidine, yielding after seven days' heating a small quantity of a yellow, crystalline *substance*, m. p. 148°, which is presumably ethyl 3-phenyl-5-*p*-dimethylaminostyryl*cyclo*hexan-1-one-2-carboxylate; when heated for two hours with alcoholic sodium ethoxide, however, the two substances react to form ethyl 3-phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate, which can only be isolated as the *benzoyl* derivative, m. p. 170—171°. A mixture of benzylidenecinnamylideneacetone, ethyl acetoacetate, and a little piperidine yields *ethyl 3-phenyl-5-β-styrylvinyl*cyclo*hexan-5-ol-1-one-2-carboxylate*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C(OH){<}{\begin{matrix}CH_2{\cdot}CHPh\\CH_2\text{——}CO\end{matrix}}{>}CH{\cdot}CO_2Et,$$

m. p. 144—145°, or *ethyl 3-phenyl-5-β-styrylvinyl-Δ^5-*cyclo*hexen-1-one-2-carboxylate*, m. p. 145°, accordingly as it is heated on the water-bath for a day and kept for several days or is heated with alcohol for the same time. C. S.

Action of Hydroxylamine on Ketones of the Type CHR:CH·CH:CH·CO. ROBERTO CIUSA and A. BERNARDI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 58—62. Compare Abstr., 1907, i, 62).—Styryl methyl ketone yields the oxime of m. p. 117° already known; phenyl styryl ketone, two isomeric hydroxylamineoximes, which are also known. Benzylidenecinnamylideneacetone gives a *hydroxylamineoxime*, m. p. 165°. Benzylidenepyruvic acid yields an *oxime*, m. p. 168°. When the sodium salt of cinnamylidenepyruvic acid is acted on by hydroxylamine in the absence of sodium acetate, it yields the *sodium* salt of an *oxime*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}C({:}NOH){\cdot}CO_2Na$, from which, by loss of carbon dioxide, cinnamylideneacetonitrile is formed. In the presence of sodium acetate, however, an *oxime*, $C_{28}H_{26}O_9N_2$, m. p. 216—218°, is produced, probably by the union of two molecules of the esterified acid with two molecules of hydroxylamine. Ethyl cinnamylidenepyruvate gives an *hydroxylamineoxime*, $C_{26}H_{34}O_9N_4$, m. p. 213°, formed from 2 mols. of ester and 4 mols. of hydroxylamine.

The formation of oximes in some cases, and of hydroxylamineoximes in others is due to the different velocities with which the addition of hydroxylamine proceeds at the carbonyl group and at the system of double linkings. If the former is the greater, an oxime is formed, which although unsaturated does not react with hydroxylamine. The velocity of oxime formation is diminished when a methyl group of the ketone is replaced by a phenyl group (Petrenko-Kritschenko, Abstr., 1906, ii, 341), and this explains the formation of oximes from styryl methyl ketone and cinnamylideneacetone (Abstr., 1907, i, 62), whilst phenyl styryl ketone and cinnamylideneacetophenone yield hydroxylamineoximes. R. V. S.

Displacement of Alkyl Groups under the Influence of Aluminium Chloride. Acetyldiphenylmethanes and their Derivatives. Constitution of Some Derivatives of Diphenylmethane. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], **7**, 789—796, 796—800).—Most of the data published in these two papers have been

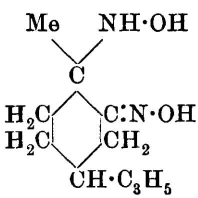
given already (Abstr., 1908, i, 277, 657). By the action of acetyl chloride on diphenylmethane in presence of aluminium chloride there is formed, in addition to 4-acetyl and 4 : 4′-diacetyl derivatives of the hydrocarbon, some acetophenone and a substance, m. p. 125°, which forms colourless crystals and appears to be a *4 : 4′-diacetylbenzyl-diphenylmethane*, $CH_2Ph \cdot C_6H_3Ac \cdot CH_2 \cdot C_6H_4Ac$. Details of the method of carrying out the operation and of separating and purifying the products are given.

4-Acetyldiphenylmethane, b. p. 209—210°/15 mm., forms colourless crystals from alcohol.

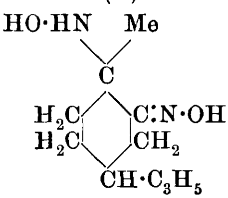
4 : 4′-Diacetyldiphenylmethane, b. p. 270—271°/15 mm., forms colourless crystals from warm alcohol. Its constitution is established by the observation that on oxidation with sodium hypobromite it yields benzophenone-4 : 4′-dicarboxylic acid, identified by means of its methyl ester, m. p. 231° (compare Limpricht, Abstr., 1900, i, 598).

T. A. H.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. I. *d*-Limonene-*o*-hydroxylamineoxime. GUIDO CUSMANO (*Gazzetta*, 1910, **40**, i, 602—613. Compare this vol., i, 182).—By the action of hydroxylamine on both *a*- and *β*-*d*-limonene bisnitrosochlorides, the same two *cis-trans*-isomeric hydroxylamineoximes (I. and II.) are obtained, and in addition a monoacidic base, $C_{10}H_{21}O_3N_3$. Whichever nitrosochloride is employed, one of the isomerides appears in excess of the other; it has a positive optical rotation, and is therefore called the *a*-form. Like the isomeride hydroxylaminocarvoxime (compare Harries and Mayrhofer, Abstr., 1899, i, 624), the two substances are soluble in acids and in alkalis, and reduce Fehling's solution in the cold, but they are stable towards nitrous acid, do not give oxidation products, and do not condense with aldehydes. In alkaline solution they are converted rapidly into a salt (decomposed by carbon dioxide) of an isomeric yellow compound, which is soluble in acids, but does not reduce Fehling's solution, and, moreover, gives a blue coloration with diphenylamine and a violet coloration with phenol. By the action of acids the compound is converted into the original hydroxylamineoxime.



(I.)



(II.)

a-Limonenehydroxylamineoxime hydrochloride, $C_{10}H_{16}O_2N_2,HCl,H_2O$, forms large, prismatic crystals, m. p. 142°, $[a]_D^{27}$ − 35·30°. When kept in a vacuum desiccator it loses a molecule of water, and then has m. p. 153° (decomp.). The free *a-hydroxylamineoxime*, $C_{10}H_{18}O_2N_2$, forms large, colourless, prismatic crystals, which soften towards 145° and decompose at 150°; it has $[a]_D^{27}$ + 17·73°. The *β-hydroxylamineoxime* is obtained in very small quantity along with the *a*-form. It has m. p. 173° (decomp.), and gives a *hydrochloride*, m. p. 152°. In the above preparation the *hydrochloride* of a base, $C_{10}H_{21}O_3N_3,HCl$, is also formed in small quantity. It crystallises in needles or flat prisms,

m. p. about 212° (decomp.); $[\alpha]_D^{27}$ −57·88°. The *base*, $C_{10}H_{21}O_8N_3$, has m. p. towards 210° (decomp.), and scarcely reduces Fehling's solution in the warm. All the above compounds are similarly obtained from *β-d*-limonene bisnitrosochloride. The yellow *isomeride* of the α-hydroxylamineoxime is readily formed from the latter substance, especially if impure or in solution. It is prepared by precipitating alkaline solutions of the substance with carbon dioxide. It has m. p. 167·5° (decomp.), and the molecular weight required by the formula $C_{10}H_{18}O_2N_3$. Treatment with acids converts it into the α-hydroxylamineoxime. When this change is effected with ethereal hydrogen chloride, a *substance*, $C_{10}H_{20}O_2N_2Cl_2$, is also obtained in yellow prisms, m. p. 130° (decomp. explosively). It is unstable, gives an intense blue diphenylamine reaction, does not dissolve in cold alkalis, and does not yield the hydroxylamineoxime when treated with hydrogen chloride in ether. R. V. S.

Mechanism of the Opening of the *cyclo*Butane Ring in Derivatives of Pinene. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 63—68. Compare this vol., i, 574, and preceding abstract).—α-Pinenehydroxylamineoxime yields, with alkalis, nitrosopinene, with acids, hydroxydihydrocarvoxime. According to Wallach's theory of the mechanism of the opening of the *cyclo*butane ring in pinene and in sabinene derivatives (Abstr., 1908, i, 429), the formation of nitrosopinene as an intermediate product would be expected in the latter case, but the author shows that nitrosopinene does not yield hydroxydihydrocarvoxime when acted on by acids. Similarly, the salts of pinene*iso*nitroamineoxime yield, when treated with alkalis, both nitrosopinene and hydroxypinocamphoneoxime. Neither of these compounds can be converted into the other under the conditions of the experiment, but dilute acids transform hydroxypinocamphoneoxime into the isomeric hydroxydihydrocarvoxime. It appears, therefore, that Wallach's theory is untenable in this case, for which the author provides the explanation that the loss of the elements of water so disturbs the molecule as to cause rupture of the bridge at the same time, whilst the displacement of hyponitrous acid does not.

R. V. S.

Constitution of Fenchone. IV. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 807—810).—In previous papers (this vol., i, 572, 573, 627) the steps in the gradual degradation of fenchone to *apo*fenchene have been detailed, and in this communication an account is given of the oxidation of this hydrocarbon, on which a preliminary paper has been already published (Abstr., 1908, i, 193).

The products of the oxidation of *apo*fenchene by alkaline permanganate are (1) a neutral substance, probably a glycol; (2) a small quantity of a mixture of fatty acids, and acids possessing a pyruvic odour; (3) a mixture of acids (b. p. 70—160°/10 mm.) containing 90% of *iso*propylsuccinic acid, and (4) a mixture of acids (b. p. 160—165°/10 mm.). The fourth fraction contains three acids: (1) a hydroxy-acid, yielding on oxidation by lead peroxide and sulphuric acid a ketonic substance of the type R·COMe; (2) a ketonic acid, furnishing a *semi-*

carbazone, m. p. 140°, and (3) a ketonic acid, yielding a *semicarbazone*, $C_{10}H_{19}O_3N_3$, and which on oxidation with sodium hypobromite gives β-*iso*propylglutaric acid. As already indicated (*loc. cit.*), these results support Semmler's formula for fenchone. T. A. H.

Causes of Geranic Odours. GÉZA AUSTERWEIL and G. COCHIN (*Compt. rend.*, 1910, **151**, 440—441. Compare this vol., i, 572).—The group :CH·CRR′·OH appears to be necessary for the presence of a geraniol odour. 1-*Methylgeraniol*, b. p. 105—106°/18 mm., prepared by the application of Grignard's reaction to citral, has a pronounced odour of pelargonium leaves; this is scarcely modified by the introduction of a second methyl group. 1 : 1-*Dimethylgeraniol*, b. p. 104°/16 mm., was obtained by oxidising the foregoing compound and submitting the ketone to Grignard's reaction. The odour of 1-ethylgeraniol and 1 : 1-*diethylgeraniol*, b. p. 123—125°/20 mm., resembles that of the primary alcohol. 1-iso*Butylgeraniol*, b. p. 115°/26 mm., and 1-*phenylgeraniol*, b. p. 135—138°/22 mm., have a less intense odour, that of the latter being somewhat rose-like. *Methyl*cyclo*geraniol*, b. p. 98°/20 mm., has scarcely any geraniol odour. W. O. W.

Oil of Copaiba. ERNST DEUSSEN and ALFRED HAHN (*Chem. Zeit.*, 1910, **34**, 873).—The caryophyllene from oil of copaiba is not a definite product, but yields on distillation several fractions with an increasing rotatory power, thus distinguishing it from the caryophyllene obtained from oil of cloves, the higher fractions of which show a decreasing rotatory power. No permanent blue coloration is obtained by acting on the caryophyllene from copaiba with nitrosyl chloride, whereas that from cloves yields a blue nitrosite.

Both oils, however, contain sesquiterpenes of a preponderating bicylic nature. L. DE K.

Gurjun Oil (So-called East Indian Copaiba Oil). ERNST DEUSSEN and HANS PHILLIPP (*Chem. Zeit.*, 1910, **34**, 921—923).—An investigation as to the nature of gurjun oil, which seems to belong to the series of sesquiterpenes.

Utz's statement that gurjun oil has a much higher boiling point than oil of copaiba is not quite correct, and this fact should be taken into consideration when testing copaiba balsam for gurjun balsam and operating, according to Utz, on the distillate. The colour reaction (whether working on the balsam itself or on the volatile oil therefrom) due to Turner and approved of by Utz, and again strongly recommended by the authors, is as follows: 3 to 4 drops of the sample of copaiba balsam are dissolved in 3 c.c. of glacial acetic acid, 1 drop of a 10% solution of sodium nitrite is added, and the mixture is carefully poured on to 2 c.c. of sulphuric acid. In presence of gurjun balsam a dark violet colour will be noticed in the acetic acid layer.

L. DE K.

New Components of Oil of Jasmine Flower. F. ELZE (*Chem. Zeit.*, 1910, **34**, 912).—In addition to the substances found in oil of jasmine flower by Hesse (Abstr., 1899, i, 377, 441; 1900, i, 48, 454;

1901, i, 220, 732), the author finds that it contains *p*-cresol and geraniol. L. DE K.

[Essential] Oil of Robinia Pseudocacia. F. ELZE (*Chem. Zeit.*, 1910, **34**, 814).—The author prepared a specimen of the oil by extracting the blossoms of the plant with very volatile solvents; the crude oil was then purified by treatment with alcohol. The oil had D^{15} 1·05, and the ester content calculated as methyl anthranilate amounted to 9%. The alcoholic solution had a distinct bluish fluorescence, and contained much indole. Under 5 mm. pressure, the oil passed over between 60° and 150°.

When submitted to the usual tests for essential oils, it was found to contain benzyl alcohol, α-terpineol, heliotropine, methyl anthranilate, linalool, indole, and ketone or aldehyde substances having the odour of peaches. The presence of nerol is also probable, and pyridine bases could be isolated. L. DE K.

Nerol and Farnesol in Java Canang Oil. F. ELZE (*Chem. Zeit.*, 1910, **34**, 851).—The oil contains about 0·2% of nerol and about 0·3% of farnesol. L. DE K.

Honduras Balsam. ALEXANDER TSCHIRCH and J. O. WERDMÜLLER (*Arch. Pharm.*, 1910, **248**, 420—430).—A pale Honduras balsam, represented by three samples having D 1·0886, 1·0905, and 1·0884 respectively, and a pronounced odour of storax, has mean acid number 32·67 and saponification number 173·2. The balsam is dissolved in ether and shaken with 1% sodium carbonate, whereby cinnamic acid is extracted together with an ester which yields cinnamic acid and honduro-resinol by hydrolysis. The ethereal solution is next treated with 1% potassium hydroxide, whereby a further quantity of honduroresinyl cinnamate is obtained, and also a *substance*, $(C_{38}H_{38}O_4)_x$, which melts above 300°, does not respond to the phytosterol reactions, and shows the properties of a resin; it is called β-honduroresin. The ethereal solution is finally evaporated, leaving a yellow oil (so-called "cinnamëin") representing more than half the weight of the balsam. A portion of the oil yields by distillation cinnamic acid and an oil from which a small quantity of a hydrocarbon, *honduran*, C_8H_{10}, b. p. 154—155°, can be isolated. Another portion of the "cinnamëin" is hydrolysed by 1% potassium hydroxide, whereby cinnamyl alcohol, cinnamic acid, honduran, a *hydrocarbon*, $(C_3H_4)_x$, b. p. 140—155°, and distyrene are produced.

A dark Honduras balsam, represented by two samples, D 1·0897 and 1·0915, has acid number 29·9 and saponification number 153·9. It has been examined in the preceding way. The sodium carbonate extract contains cinnamic acid and the cinnamate of a *honduroresinol*, $(C_{16}H_{26}O_2)_x$, m. p. 141°. The potassium hydroxide extract contains cinnamic acid, honduroresinyl cinnamate, and a *resin*, m. p. 169—172°, which is not identical with β-honduroresin. The "cinnamëin" is hydrolysed by aqueous potassium hydroxide, and then distilled with steam. The non-volatile oil is dissolved in alcohol and cooled by solid carbon dioxide, whereby crystals are obtained, which are collected,

washed with alcohol, and treated with warm petroleum. The portion insoluble in the petroleum is a *resin*, m. p. 163°. When cooled in carbon dioxide, the petroleum solution deposits crystals of an unsaturated dihydric alcohol, *hondurol*, $C_{17}H_{16}O_2$, m. p. 42·5°, which forms a *dibenzoate*, m. p. 38°. The alcoholic mother liquor contains phenylpropyl alcohol and distyrene. C. S.

Cabureiba Balsam. ALEXANDER TSCHIRCH and J. O. WERDMÜLLER (*Arch. Pharm.*, 1910, **248**, 431—432).—Schaer has recently described a rare balsam obtained from Brazil, and probably identical with Piso's cabureiba balsam (Guibourt's baume de Pérou brun or rouge en coques). Its ethereal solution yields to 1% sodium carbonate, benzoic (but not cinnamic) acid and a resinous substance, from which, after hydrolysis by 1% potassium hydroxide, benzoic acid, vanillin, and a *cabureibaresinotannol*, $C_{14}H_{18}O_4$, have been isolated. The balsam does not contain a "cinnameïn." C. S.

Benin Copal. M. KAHAN (*Arch. Pharm.*, 1910, **248**, 433—442).—Benin copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 60%, and ether 45·5%. The dried substance sinters at 120°, and forms a clear, transparent mass at 166°. It has acid number 101·15 (direct) and 118·75 (indirect), saponification number 134·4 (cold, after twenty-four hours), 143·5 (cold, after forty-eight hours), 149·8 (hot, after one hour), 146·3 (hot, after two hours), and iodine number 61·02. It does not yield succinic acid by dry distillation. An ethereal extract of Benin copal is shaken successively with 1, 2, and 5% ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution, after removal of the ether, is distilled with steam, whereby an ethereal oil, b. p. 180—256°, and a yellow resin, *a-benincopaloresin*, m. p. 164—166°, are obtained. The ammonium carbonate extract contains *benincopalic acid*, $C_{17}H_{32}O_4$, m. p. 137°, acid number 183·4 (direct) and 180·6 (indirect), saponification number 194·6 (cold, after twenty-four hours), 196·0 (cold, after forty-eight hours), 196·7 (hot, after one hour), 200·2 (hot, after two hours), iodine number 83·43, which forms a lead salt insoluble in alcohol. The sodium carbonate extract contains *a-benincopalolic acid*, $C_{13}H_{32}O_6$, m. p. 81°, acid number 191·8 (direct) and 188·9 (indirect), saponification number 198·3 (cold) and 197·4 (hot), iodine number 87·24, and *β-benincopalolic acid*, $C_{20}H_{30}O_2$, m. p. 119°, acid number 185·2 (direct) and 184·1 (indirect), saponification number 193·3 (cold) and 194·6 (hot), iodine number 84·84; the lead salts of the two acids are insoluble in alcohol, but the former acid dissolves in glacial acetic acid. The potassium hydroxide extract contains *benincopalenic acid*, $C_{27}H_{48}O_2$, m. p. 101°, acid number 147·0 (direct) and 145·6 (indirect), iodine number 63·88.

The residue of Benin copal insoluble in ether is dissolved almost completely by a mixture of ether and alcohol. The solution, after being shaken with 1% potassium hydroxide, contains *β-benincopaloresin*, $C_{12}H_{30}O_{10}$, a white, amorphous substance. The potassium hydroxide extract contains *a-benincopalinic acid*, $C_{21}H_{30}O_3$, m. p. 187°, acid number 172·2 (direct) and 170·8 (indirect), saponification number 180·6 (cold) and 177·8 (hot), iodine number 76·51; *β-benincopalinic*

acid, $C_{15}H_{28}O_3$, m. p. 193—197°, acid number 216·3 (direct) and 216·3 (indirect), iodine number 97·79, and *γ-benincopaloresin*, $C_{13}H_{26}O_4$, m. p. 192—195°; the last is insoluble in alcohol, whilst of the two acids the former yields a lead salt which is insoluble in alcohol. C. S.

Accra Copal. M. KAHAN (*Arch. Pharm.*, 1910, **248**, 443—450).—Accra copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 54% and ether 50%. The substance has m. p. 106—156°, acid number 121·8 (direct) and 126·4 (indirect), saponification number 133·4 (cold) and 140·0 (hot), and iodine number 58·54.

An ethereal extract of Accra copal is shaken successively with ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution contains *α-accracopaloresin*, $C_{15}H_{36}O_6$, m. p. 178—180°, and an ethereal oil, b. p. 164—266°. The ammonium carbonate extract contains *accracopalic acid*, $C_{21}H_{34}O_3$, m. p. 104—106°, acid number 177·5 (direct) and 175·0 (indirect), saponification number 180·7 (cold) and 180·6 (hot), iodine number 75·31. The sodium carbonate extract contains *α-accracopalolic acid*, $C_{18}H_{30}O_2$, m. p. 152—155°, acid number 194·6 (direct) and 192·5 (indirect), saponification number 195·3 (cold) and 196·4 (hot), iodine number 85·49, and *β accracopalolic acid*, $C_{19}H_{32}O_2$, m. p. 144—148°, acid number 189·0 (direct) and 186·9 (indirect), saponification number 194·6 (cold) and 195·3 (hot), iodine number 86·86. The potassium hydroxide extract contains *α-accracopalenic acid*, $C_{10}H_{20}O_2$, m. p. 142—146°, and *β-accracopalenic acid*, $C_{12}H_{20}O_3$, m. p. 150—152°, acid number 246·4, which are separated by lead acetate.

The residue of the Accra copal insoluble in ether is dissolved in a mixture of ether and alcohol, and the solution is shaken with 1% potassium hydroxide; the ethereal alcoholic solution retains *β-accracopaloresin*, $C_{13}H_{26}O_3$, m. p. 197—199°, whilst the alkaline extract contains *accracopalinic acid*, $C_{14}H_{26}O_3$, m. p. 122—124°, acid number 214·9 (direct) and 214·2 (indirect), saponification number 226·8 (cold) and 228·2 (hot), iodine number 98·29, and *γ-accracopaloresin*, $C_{10}H_{20}O_3$, m. p. 184—186°, which is insoluble in alcohol. C. S.

Manila Copal. GEORGE F. RICHMOND (*Philippine J. Sci.*, 1910, [*A*], **5**, 177—201).—It is shown that the Manila copal produced in the Philippines is of two kinds, "recent" and semifossil," and is derived from a single species, *Agathis alba* (*Dammara orientalis*). The constants of the two kinds of resin are quite similar, and they both consist of a mixture of resin acids with a lactone (?), neutral unsaponifiable resin, and more or less volatile oil. The only well-defined solid product obtained from the resin is a crystalline acid of the formula $C_{10}H_{15}O_2$. On distillation in steam the resin yields volatile oil in quantity, which depends partly on the age of the resin and partly on its physical condition. The volatile oil, D_4^{15} 0·865, n_D^{30} 1·4648, $[\alpha]_D^{30}$ −26·55°, contains pinene. The resin dissolves completely in alcohol, and addition of potassium hydroxide to such a preparation yields (*A*) a solution containing volatile oil and soluble

potassium resinates, and (*B*) a precipitate containing insoluble potassium resinates and some neutral resin.

From *A* the following substances were obtained: (1) a lemon-yellow, volatile oil possessing a terpene-like odour; (2) an *acid*, $C_{10}H_{15}O_2$, m. p. 185—187°, which is dextrorotatory and crystallises from dilute alcohol in colourless needles, and (3) an amorphous *acid*, $C_{22}H_{34}O_4$, which can be distilled almost unchanged at a pressure of 3—5 mm., yielding a clear, amber-coloured product.

From *B* there were isolated (1) an amorphous *acid*, $C_{32}H_{50}O_4$, m. p. above 220°; (2) a *lactonic* substance, which on digestion with hot aqueous solutions of potassium hydroxide furnishes the potassium salt of a resin acid similar to that yielding the insoluble resinate referred to above, and (3) neutral unsaponifiable resin. These results, especially as regards the properties of the acids, are not in accordance with those recorded by Tschirch and Koch for Manila copal derived from *Dammara orientalis* (Abstr., 1902, i, 478).

On dry distillation the copal yielded about 70% of greenish-yellow oil, b. p. 140—350°, and left a pitch-like residue (compare succeeding abstract). On "melting" various samples of the resin at temperatures ranging from 250—325°, the loss varied from 13·3 to 17·4%. The "melted" resin was similar in composition to the raw material, but contained less neutral resin, so that the latter only appears to undergo change in the ordinary process of making copal varnish. The remainder of the paper deals with copal varnish manufacture.

T. A. H.

Destructive Distillation of Manila Copal. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [*A*], 5, 203—217. Compare preceding and succeeding abstracts).—On heating, Manila copal froths until the temperature reaches 330°, when the resin melts and quiet ebullition sets in. Up to 330° the products evolved include resin oil, pinene, *β*-pinene, limonene, dipentene, camphene, water, formic and acetic acids, methyl alcohol, acetone, formaldehyde, pyruvaldehyde, furfuraldehyde, carbon dioxide, acraldehyde (?), and saturated and unsaturated hydrocarbons. Above 330°, considerable quantities of carbon monoxide and some ethylene and propylene are formed, but the other products of this further stage in destructive distillation were not studied. The remainder of the paper deals with (1) the effect of heat in rendering Manila copal soluble and suitable for varnish manufacture, and (2) its behaviour with various solvents.

T. A. H.

Oxidation of Manila Copal by the Air. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [*A*], 5, 219—227. Compare two preceding abstracts).—The well-known fact that the older copal resins ("fossil" copals) are better suited for varnish manufacture than the "recent" kinds has led the author to investigate the changes which take place when Manila copal is exposed to air and light. The results show that the resin absorbs oxygen somewhat rapidly, forming organic peroxides (compare Fahrion, Abstr., 1902, i, 165; 1904, i, 332; 1907, i, 329), and evolves carbon dioxide, formaldehyde, formic acid, and hydrogen

peroxide. The evolution of carbon dioxide is probably due to the formation and subsequent decomposition of peroxides, both in the cases of Manila copal and colophony. These changes are accompanied by an increase in the Koettstorfer number of the resin. The change in the Koettstorfer number, which accompanies prolonged maceration of many resins in potassium hydroxide in alcohol, is, however, not due to oxidation effects during the experiment, but probably to the gradual saponification of lactones and the breaking down of organic peroxides. The oxidation of Manila copal is accelerated by sunlight. Under certain conditions the resin gives off vapours which affect a photographic plate. The mixed resin acids of Manila copal show similar changes on exposure to air, but more slowly. T. A. H.

Oleo-Resin of Pinus insularis. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [*A*], 5, 229—231).—The turpentine oil distilled from this oleo-resin had D_{30}^{30} 0·8593, n_D^{30} 1·4656, $[\alpha]_D$ +26·5 at 30°, distilled to the extent of 96% between 154° and 165·5°, and consisted mainly of pinene.

The colophony left on distillation of the oleo-resin consisted almost entirely of abietic acid, m. p. 154—156°, had Koettstorfer number 170·2, and gave the Liebermann-Storch reaction. T. A. H.

Preparation of True Arbutin. HENRI HÉRISSEY (*Compt. rend.*, 1910, 151, 444—447; *J. Pharm. Chim.*, 1910, [vii], 2, 248—253).—Fifteen grams of commercial arbutin (containing methylarbutin) are dissolved in 95% alcohol (500 c.c.) and treated with 10 grams of potassium hydroxide in 125 c.c. of alcohol. When clear, the supernatant liquid is removed, and the crystalline precipitate washed with alcohol (20 c.c.), dissolved in 75 c.c. of boiling alcohol and acetic acid (7 c.c.), and treated with calcium carbonate (5 grams). After removing the alcohol, the residue is lixiviated with water (100, 50, and 50 c.c.). The filtrate is treated with calcium carbonate (2 grams), evaporated to dryness, and the product crystallised from ethyl acetate. Pure arbutin crystallises with $1H_2O$, and is identical with the glucoside obtained from the pear tree by Bourquelot (this vol., ii, 742). The anhydrous substance has $[\alpha]_D$ −63·45°. W. O. W.

A New Glucoside Hydrolysed by Emulsin in Menyanthes trifoliata. MARC BRIDEL (*J. Pharm. Chim.*, 1910, [vii], 2, 165—167).—The glucoside, which it is proposed to call *meliatin*, m. p. 222° (corr.), $[\alpha]_D$ −81·94° in alcohol, is crystalline. Its solutions are hydrolysed by emulsin, becoming bluish-green and dextrorotatory, and producing a reducing sugar. It is not identical with Kromayer's menyanthin (*Arch. Pharm.*, 1865, 174, 35, and Lendrich, Abstr., 1892, 1262). T. A. H.

The Chlorophyll Group. VII. Chlorophyllan, *allo*Chlorophyllan, and Chlorophyllpyrrole. HENRYK MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1910, 27, 246—260. Compare this vol., ii, 362).—It is claimed that the substances described under the name of chlorophyllan, phyllogen, and phæophytin are identical.

They were prepared by the methods described by Schunk and Marchlewski and Willstätter, and the various preparations yielded the same amount of phytol on hydrolysis, and yielded chlorophyllanic acids similar to the phytochlorins of Willstätter. A preparation was also obtained which did not agree in properties with Willstätter's phytochlorin-*d*. Chlorophyllan also contains in small quantities (especially that derived from maple leaves) another product, *allo*-chlorophyllan, of which the authors give some spectrum absorption measurements. They have also succeeded in preparing from chlorophyllpyrrole, azo-colouring matters with benzenediazonium chloride identical with those obtained from hæmopyrrole. S. B. S.

Benzoyleuxanthone. ERNST ZERNER (*Monatsh.*, 1910, **31** 797—798).—Graebe and Ebrard (Abstr., 1882, 1301) describe dibenzoyleuxanthone as yellow or brown, m. p. 214°. On benzoylating euxanthone with benzoyl chloride and potassium hydroxide, the dibenzoyl derivative is obtained colourless, m. p. 221—222° (corr.), together with about 10% of yellow *monobenzoyleuxanthone*, m. p. 156—159° (corr.), in which the benzoyl group occupies position 7. On benzoylating in acid solution, only dibenzoyleuxanthone results.
E. F. A.

[Preparation of Halogen Derivatives of 6-Amino-3-keto-(1)-thionaphthen and Nitroisatins.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 221529 and 221530).—When the products obtained by condensing 6-amino-3-keto-(1)-thionaphthen in acetic acid solution with nitroisatins or amino-oxindoles are treated with halogens either with or without previous reduction, brownish-yellow dyes are obtained.

6-*Amino-3-keto-(1)-thionaphthen*, m. p. 165°, is a brownish-grey powder, soluble in hot water.

The nitration of isatin with fuming nitric acid (D 1·5) yields a *nitroisatin*, which crystallises from acetic acid in yellow needles, m. p. 253—255°; potassium nitrate with concentrated sulphuric acid may also be employed, but under these conditions the product has m. p. 248—250°.

The second patent deals with the products obtained when the 6-amino-3-keto-(1)-thionaphthen in the foregoing condensation is replaced by *m*-acetylaminophenylthioglycol-*o*-carboxylic acid, the components being heated together during three hours in the presence of acetic anhydride; the *product* is a brown powder, which becomes yellow on treatment with sodium hyposulphite, and on halogenation yields vat dyes. The reduction of these compounds previous to halogenation is also described in the patents. F. M. G. M.

Ergoxanthein. WILLIAM T. WENZELL (*Amer. J. Pharm.*, 1910, **82**, 410—416).—The author does not consider that the preparation of the alkaloids of ergot in a purer form justifies the supersession of the names ecboline and ergotine originally applied by him to these alkaloids (*Amer. J. Pharm.*, 1864, **36**, 193; compare Kobert, Abstr., 1885, 821; Barger, Trans., 1907, **91**, 337, and Barger and Dale, Abstr., 1907, i, 79).

Ergoxanthein was prepared from Squibb's fluid extract of ergot by shaking this with ether after preliminary purification with alcohol and chloroform. It is an orange-yellow, amorphous substance, giving blood-red solutions with alkalis, developing a deep orange colour with nitric acid and a blood-red coloration with sulphuric acid. It gives an orange-yellow precipitate with lead acetate and a yellow precipitate with phosphotungstic acid. The absorption spectra of solutions of ergoxanthein are recorded which may be of value for the estimation and toxicological detection of ergot. The substance is physiologically active, and causes a rise in blood pressure. T. A. H.

Hydroxylupanine. A. BECKEL (*Arch. Pharm.*, 1910, **248**, 451—457).—The properties and behaviour of natural hydroxylupanine, already recorded by Bergh (*Arch. Pharm.*, 1904, **242**, 416) are confirmed, and the formation of *d*-lupanine by reduction is proved conclusively by an examination of the aurichloride, platinichloride, and thiocyanate. C. S.

Compounds of α-Naphthylcarbamide with some Physiologically Important Substances. CARL NEUBERG and ELSE HIRSCHBERG (*Biochem. Zeitsch.*, 1910, **27**, 339—347).—This reagent gives sparingly soluble α-naphthylhydantoic acids with amino-acids, and α-naphthylurethanes with alcohols and phenols. The former can be prepared by shaking aqueous solutions of the reacting substance together in the presence of alkalis; the latter must be prepared in absence of water, and are obtained by heating the reacting substances together. The following substances were obtained: *glyceryl tri-α-naphthylcarbamate*,

$$C_{10}H_7\cdot NH\cdot CO_2\cdot CH_2\cdot CH(CO_2\cdot NH\cdot C_{10}H_7)\cdot CH_2\cdot CO_2\cdot NH\cdot C_{10}H_7,$$

m. p. 279—280°; the *di-α-naphthylurethane* of glyceric acid,

$$C_{10}H_7\cdot NH\cdot CO_2\cdot CH_2\cdot CH(CO_2H)\cdot CO_2\cdot NH\cdot C_{10}H_7,$$

m. p. 289—290°; *phenyl α-naphthylcarbamate*, m. p. 136—137°; o-*tolyl α-naphthylcarbamate*, m. p. 145°; m-*tolyl α-naphthylcarbamate*, m. p. 135—136°; p-*tolyl α-naphthylcarbamate*, m. p. 150—151°; *carvacryl α-naphthylcarbamate*, m. p. 287—288°; *saligenyl α-naphthylcarbamate*, m. p. 283°; *cinnamyl α-naphthylcarbamate*, m. p. 119—120°; *menthyl α-naphthylcarbamate*, m. p. 128°; l-*bornyl α-naphthylcarbamate*, m. p. 132°; iso*bornyl α-naphthylcarbamate*, m. p. 129°; *α-terpinyl α naphthylcarbamate*, m. p. 151—152°; cyclo*hexyl α-naphthylcarbamate*, m. p. 139—140°; *furfuryl α-naphthylcarbamate*, m. p. 133°; *cholesteryl α-naphthylcarbamate*, m. p. 175—176°; *α-naphthylcarbamo*-d-*glucosamine*, $OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot CH(CHO)\cdot NH\cdot CO\cdot NH\cdot C_{10}H_7$, m. p. 234—236°; *α-naphthylcarbamidoacetaldehyde*,

$$C_{10}H_7\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CHO,$$

amorphous. S. B. S.

Substituted Rodanic Acids and their Aldehyde Condensation Products. X. RUDOLF ANDREASCH (*Monatsh.*, 1910, **31**, 785—795. Compare Abstr.,.1908, i, 683).—*Ammonium dithiocarbaminoacetate*,

$$NH_4\cdot S\cdot CS\cdot NH\cdot CH_2\cdot CO_2\cdot NH_4,$$

prepared by the interaction of glycine, carbon disulphide, and alcoholic ammonia, forms colourless needles, m. p. 110° (decomp.).

Ammonium-a-dithiocarbaminopropionate, prepared in a similar manner from alanine, has m. p. 128—129° (decomp.). It reacts with ethyl chloroacetate, forming *a-rhodaninepropionic acid*,

$$CO_2H\cdot CHMe\cdot N<\begin{matrix} CS\cdot S \\ CO\cdot CH_2 \end{matrix},$$

separating in granular crystals, m. p. 147°. Condensation products with aldehydes are formed on heating the components in acetic acid.

β-Benzylidene-a-rhodaninepropionic acid forms bright yellow granules or needles, m. p. 191°. *β-Dimethylaminobenzylidene-a-rhodaninepropionic acid* forms a crust of dark reddish-brown crystals, m. p. 210—220°; it dyes the skin, wool, and silk orange-red, but the colour is not fast. *β-*p*-Hydroxybenzylidene-a-rhodaninepropionic acid* forms a crust of light chrome-yellow needles, which sinter at 190°, m. p. 205—210°, forming a red sublimate.

β-Methylenedioxybenzylidene-a-rhodaninepropionic acid, prepared by condensation with piperonal, forms orange-yellow granules or a yellow, crystalline powder, m. p. 197—199°.

Rhodanineglycylglycine, $CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot N<\begin{matrix} CS\cdot S \\ CO\cdot CH_2 \end{matrix}$, is prepared by the interaction of glycylglycine, ammonia, and carbon disulphide, the corresponding *dithiocarbamate* being first formed and immediately condensing with ethyl chloroacetate. A honey-yellow syrup was obtained, which condensed with benzaldehyde to *benzylidene-rhodanineglycylglycine*. It crystallises in greenish-yellow plates or needles, m. p. 190° (sinters at 180°).

In the case of asparagine, aspartic and glutamic acids, and leucine, both the rhodanines and their aldehyde condensation products could only be obtained as syrups. E. F. A.

Formation of Imino-ethers by Direct Alkylation of Acid Amides with Methyl Sulphate. MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, **2**, 37—45).—Imino-ethers may be obtained directly from the free acid amides by alkylation with methyl sulphate at temperatures below 100°, showing that the amide itself may react in the iminohydrin form, just as does its silver salt. Both aliphatic and aromatic acid amides, as well as the thio-acid amides, react in this way, giving rise to the methyl hydrogen sulphates of the imino-ethers. These compounds generally separate as an oil, which may afterwards crystallise, when the amide is heated in a reflux apparatus with methyl sulphate. In some cases the imino-ether was set free by treatment with sodium carbonate solution, extracted with ethyl ether, and the hydrochloride or other salts prepared.

Thiobenziminomethyl ether methyl hydrogen sulphate, C_8H_9NS,HSO_4Me, and *thio-*p*-toluiminomethyl ether methyl hydrogen sulphate*,

$$C_9H_{11}NS,HSO_4Me,$$

were prepared from thiobenzamide and thio-*p*-toluamide respectively; they form long, colourless prisms. The free ethers separated as an oil on the addition of sodium carbonate solution, but could not be isolated, as they decompose into methyl mercaptan and cyaphenine or cyatoline.

Benziminomethyl ether methyl hydrogen sulphate was obtained from

benzamide as a deliquescent substance; it could not be purified from the admixed benzamide. The hydrochloride (Abstr., 1895, i, 522) and also the *platinichloride*, $(C_8H_{10}ON)_2PtCl_6$, were prepared.

o-*Nitrobenziminomethyl ether*, $C_8H_9O_3N_2$, was obtained from *o*-nitrobenzamide in colourless crystals, m. p. 87°. The *hydrochloride* forms slender needles, m. p. 164—165°; the *platinichloride*,

$$(C_8H_9O_3N_2)_2PtCl_6,$$

m. p. 162°, was also prepared. The hydrochloride was transformed into *o-nitrobenzamidine*, which is a yellow liquid of alkaline reactions; its *platinichloride*, $(C_7H_8O_2N_3)_2PtCl_6$, was analysed.

Benzphenyliminomethyl ether, $C_9H_{12}ON$, was obtained from acetanilide as a colourless, viscid oil. The *hydrochloride* is decomposed by water; the *platinichloride*, $(C_9H_{12}ON)_2PtCl_6$, was analysed.

Formamide gave rise to hygroscopic, scaly crystals of *formiminomethyl ether methyl hydrogen sulphate*, from which formiminomethyl ether was liberated by alkali. *Acetiminomethyl ether* is an oil, b. p. 63—65°. Qualitative proof of the formation of *propioiminomethyl ether* from propionamide was obtained. T. S. P.

Methylpyridonium Picrate. G. TOTANI and Z. HOSHIAI (*Zeitsch. physiol. Chem.*, 1910, 68, 85. Compare Abstr., 1909, ii, 327).—*Methylpyridonium picrate*, $C_5H_5NMe{\cdot}O{\cdot}C_6H_2(NO_2)_3$, crystallises from water in slender, yellow needles, m. p. 212°. Its solubility in 100 parts of solvent at the ordinary temperature is: water 1·092, alcohol 0·368, ether 0·017. J. J. S.

[Preparation of Dinitronaphthylpyridinium Derivatives.] FARBENFABRIKEN VORM. FREIDR. BAYER & Co. (D.R.-P. 222130. Compare Zincke, Abstr., 1904, i, 448).—The interaction of secondary dihydroindoles with cyanopyridinium or dinitrophenylpyridinium salts, whereby red to violet basic dyes are obtained, has previously been recorded. When the halogen-free *product*, red needles, m.p. 214°, prepared by the action of pyridine (2 mols.) on 1-chloro-2 : 4-dinitronaphthalene (1 mol.) in aqueous alcoholic solution, is treated with α-methyldihydroindole in glacial acetic acid, and hydrochloric acid dropped in, a mixture of 2 : 4-dinitro-α-naphthylamine and a dye is obtained; these are separated by extracting the latter with boiling water, and subsequently precipitating with salt; it forms a brownish-red powder.

F. M. G. M.

Racemic Liquid Compounds. ALBERT LADENBURG (*Compt. rend.*, 1910, 151, 283—284).—Four crystallisations of the *d*-camphor sulphonate of *r*-pipecoline suffice to obtain the *l*-base in a state of purity. The author shows that the freezing-point curve for mixtures of *d*- and *l*-pipecoline agrees with the existence of a racemic liquid form of this substance. W. O. W.

[Preparation of Anthraquinoneacridones.] FRITZ ULLMANN (D.R.-P. 221853).—When the anilinoanthraquinonecarboxylic acids of general formula $CO_2H{\cdot}C_6H_4{\cdot}NHR$ (where R = anthraquinone or a substituted anthraquinone residue) are treated with reagents, such as

phosphorus pentachloride and aluminium trichloride, they are converted into anthraquinoneacridones.

Anthraquinoneacridone is prepared by treating α-anilinoanthraquinonecarboxylic acid (obtained from α-nitro- or α-chloro-anthraquinone and anthranilic acid) with phosphorus pentachloride in benzene solution, and heating the red *acid chloride* thus obtained with aluminium trichloride; it crystallises from aniline in violet-red, glistening needles with a metallic lustre; its solution in concentrated sulphuric acid is red.

The *methylanthraquinoneacridone* prepared from the condensation product of anthranilic acid with 1-chloro-4-methylanthraquinone has similar properties.

The *product* obtained by treating β-anilinoanthraquinonecarboxylic acid (prepared from β-aminoanthraquinone and *o*-chlorobenzoic acid) with concentrated sulphuric acid is a very sparingly soluble, yellow powder, which dissolves in concentrated sulphuric acid with a brownish-yellow colour. F. M. G. M.

New Group of Substituted Dioxindoles. MORITZ KOHN (*Monatsh.*, 1910, **31**, 747—751).—Isatin reacts with the Grignard reagent, only one of the carbonyl groups being affected, and on hydrolysis compounds of the type $C_6H_4<\begin{matrix}CR(OH)\\NH——\end{matrix}>CO$ are obtained.

The *phenyl* derivative forms long, white, lustrous needles, m. p. 213°, to a yellowish-brown liquid.

The *benzyl* derivative crystallises in colourless needles, m. p. 171—173°.

The α-*naphthyl* derivative becomes coloured above 200°, m. p. 233°.

The p-*bromophenyl* derivative separates in wool-like needles, m. p. 193—195° (decomp.). All these substituted dioxindoles are stable in the atmosphere. E. F. A.

Conversion of Stachydrine into the Isomeric Methyl Hygrate. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1910, **67**, 324—331. Compare Willstätter, Abstr., 1902, i, 266; Willstätter and Kahn, *ibid.*, 1904, i, 235, 560).—When distilled under reduced pressure, stachydrine (this vol., ii, 743) gives a 66% yield of the isomeric methyl hygrate,

$$CH_2<\begin{matrix}CH_2\cdot CH—CO\\ \quad\;\; | \qquad\;\; | \\CH_2\cdot NMe_2\cdot O\end{matrix} \longrightarrow CH_2<\begin{matrix}CH_2\cdot CH\cdot CO_2Me\\ \quad\;\; | \\CH_2\cdot NMe\end{matrix}$$

Other products are trimethylamine and a little hygric acid.

So far it has not been found possible to transform the methyl ester into stachydrine. The *aurichloride* of the methyl ester,

$$C_7H_{14}O_2NAuCl_4,$$

crystallises in rectangular plates, m. p. 84—86°, and when boiled with excess of hydrochloric acid yields hygric acid aurichloride.

When the hydrochloride of the ethyl ester of stachydrine (containing also stachydrine hydrochloride) is distilled, the products are hygric acid, its methyl and ethyl esters, and their decomposition products.

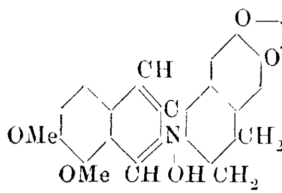
Hygric acid is non-poisonous, whereas its methyl ester is a strong poison. J. J. S.

Dissociation Constant of Tropine and its Variation with Temperature. HARALD LUNDÉN (*J. Chim. Phys.*, 1910, **8**, 331—336).—The molecular conductivities of solutions of tropine hydrochloride at 10°, 25°, and 50° show that tropine is a fairly strong base, so that hydrolytic dissociation of the hydrochloride does not occur. The molecular conductivity of free tropine at infinite dilution is calculated to be 0·17 at 10°, 0·227 at 25°, 0·326 at 50°. The variation of conductivity of the hydrochloride with temperature is in agreement with Johnston's logarithmic theorem (Abstr., 1909, ii, 854).

The dissociation constant of tropine calculated from measurements on the free base is $1·87 \times 10^{-4}$ at 10°, $2·74 \times 10^{-4}$ at 25°, and $3·89 \times 10^{-4}$ at 50°. These figures are of an entirely different order from that obtained by Veley by the colorimetric method, namely, $1·10^{-9}$ at 17° (Trans., 1909, **95**, 3). They are, however, of the same order as the dissociation of piperidine ($1·6.10^{-3}$ at 25°) and coniine ($1·3.10^{-3}$ at 25°), to which tropine is allied. The heat of dissociation of tropine calculated from the dissociation constant is negative, but appreciably greater than the negative heat of dissociation of piperidine.

The conductivity of mixtures of sodium hydroxide and tropine shows that tropine possesses no acidity, its constant of acidic dissociation being less than 10^{-14}. R. J. C.

Constitution and Derivatives of Berberine. FRANZ FALTIS (*Monatsh.*, 1910, **31**, 557—581).—When Freund and Beck's α-phenyldihydroberberine (Abstr., 1905, i, 151) is repeatedly oxidised with potassium permanganate at the ordinary temperature, appreciable amounts of 2-benzoyl-3 : 4-dimethoxybenzoic acid are formed. This reaction supports the formula (annexed formula) suggested several years ago (Abstr., 1906, i, 979) and supported recently by Perkin (Trans., 1910, **97**, 321). If berberine had the constitution originally suggested by Perkin, the product of oxidation would be 2-benzoyl-5 : 6-dimethoxybenzoic acid.



2-*Benzoyl*-3 : 4-*dimethoxybenzoic acid*, $C_6H_2Bz(OMe)_2·CO_2H$, crystallises in colourless needles, m. p. 190—191°, and is not decomposed when heated with concentrated hydrochloric acid at 150°. Its constitution follows from the fact that, when fused for two minutes with potassium hydroxide, the products are benzoic and protocatechuic acids. Boiling hydriodic acid converts the benzoylated acid into a *compound*, $C_{27}H_{20}O_8$, m. p. 223—224°. This is probably an additive compound of the 3 : 4-dihydroxy-2-benzoylbenzoic acid with 2 : 3-dihydroxybenzophenone. An impure 4-*hydroxy*-2-*benzoyl*-3-*methoxybenzoic acid*, $C_{15}H_{12}O_5$, is formed when hydrogen chloride is led through a suspension of the dimethoxy-acid in boiling hydrochloric acid for twenty-four hours.

Gadamer (Abstr., 1902, i, 555; 1905, i, 369) states that the reaction between berberine and potassium hydroxide solution is analogous to that between benzaldehyde and alkali, and that the products are

dihydroberberine and oxyberberine. The author claims that the reaction is similar to that between quinoline methiodide and alkali (Decker, Abstr., 1903, i, 516, 718), and that the products are oxyberberine and tetrahydroberberine. The reduction product differs from pure tetrahydroberberine (m. p. 167·5—168·5°) prepared from berberine by the action of zinc dust and glacial acetic acid; (*a*) its hydrochloride contains water of hydration, and (*b*) it is more readily transformed into berberine, for example, when its hydrochloride is heated at 100°.

The golden-yellow colour of Gadamer's oxyberberine is completely removed when the product is heated with zinc dust and glacial acetic acid. It is then obtained in glistening, colourless needles, m. p. 200—200·5°, with all its other properties intact. It would thus appear that only those berberine derivatives which contain a non-hydrogenated pyridine ring are coloured.

Oxyberberine hydrochloride and *hydrobromide* are readily obtained as lemon-yellow, amorphous precipitates when hydrogen chloride or bromide is passed into a chloroform solution of the base, but immediately yield colourless oxyberberine when treated with water. The hydrochloride, $C_{20}H_{17}O_5N,HCl$, softens at 200°, and melts at about 240°. The *stannichloride*, $C_{20}H_{17}O_5N,HCl,SnCl_4$, forms a stable, yellow, amorphous precipitate.

Methylnoroxyberberine, $C_{19}H_{15}O_5N$, obtained by passing hydrogen chloride into a boiling glacial acetic acid solution of oxyberberine or by heating oxyberberine hydrobromide in boiling xylene, crystallises in glistening, silky needles, m. p. 248°. It does not yield salts, and gives an intense violet-blue coloration with 50% sulphuric acid and a drop of nitric acid.

A black powder is formed when oxyberberine is boiled for a long time with hydriodic or hydrobromic acid. Methylnoroxyberberine contains a hydroxy-group, and yields an *acetyl* derivative, $C_{21}H_{17}O_6N$, m. p. 242—244°.

Bromomethylnoroxyberberine, $C_{19}H_{14}O_5NBr$, prepared by the action of bromine on a chloroform solution of methylnoroxyberberine, crystallises from hot xylene in slender needles, m. p. 239° (decomp.), and yields an *acetyl* derivative, $C_{21}H_{16}O_6NBr$, m. p. 225—227° (decomp.).

Bromine reacts with a chloroform solution of oxyberberine, yielding *bromo-oxyberberine tribromide*, $C_{18}H_{10}O_3NBr(OMe)_2,HBr,Br_2$, as golden-yellow needles, m. p. 210° (decomp.).

The tribromide when boiled with xylene yields bromomethylnoroxyberberine, and when treated with water yields *bromo-oxyberberine*, $C_{20}H_{16}O_5NBr$, which crystallises from alcohol in large, colourless prisms, m. p. 184—185°. J. J. S.

Conversion of Hydrazidines into Hydrazines. GIACOMO PONZIO (*Gazzetta*, 1910, **40**, i, 433—435).—The hydrazidines previously described (this vol., i, 443) when heated for some hours with dilute acids (10%) evolve ammonia, and are converted into the corresponding acylarylhydrazines; thus ω-aminobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) yields benzoyl-*o*-nitrophenylhydrazine,

$$COPh\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2.$$

This reaction forms an argument for the formula $NH_2\cdot CR\colon N\cdot NH_2$ in preference to $NH\colon CR\cdot NH\cdot NH_2$ for the hydrazidines. R. V. S.

Benzylidenehydrazines. HARTWIG FRANZEN and TH. EICHLER (*J. pr. Chem.*, 1910, [ii], **82**, 241—251).—At high temperatures or in boiling xylene, benzylidenehydrazines of the type $CHR\colon N\cdot NH_2$ react as such or decompose into aldazines and hydrazine, the latter of which then attacks one or more of the other substances present; for example, benzylidenehydrazine and phthalimide at 130—140° or in boiling xylene yield benzaldazine and phthalhydrazide; benzyldene-hydrazine and carbon disulphide form benzaldazine and hydirazine dithiocarbazinate, the latter being obtained by the action of hydrazine and carbon disulphide; benzylidenehydrazine and ethyl benzoate at 160—170° yield benzaldazine, benzhydrazide, and benzylidenebenz-hydrazide; benzylidenehydrazine, benzoyl chloride, and pyridine in dry ether at 0° yield benzaldazine, benzylidenebenzhydrazide, and dibenzhydrazide.

The following benzylidenehydrazines are prepared by Curtius and Franzen's method of treating aldazines with a boiling solution of hydrazine hydrate: m-*Hydroxybenzylidenehydrazine*,

$$OH\cdot C_6H_4\cdot CH\colon N\cdot NH_2,$$

m. p. 104·5° (*picrate*, m. p. 187°; *phenylthiosemicarbazide*, m. p. 194°), from m-*hydroxybenzaldazine*, m. p. 205°; p-*hydroxybenzylidenehydr-azine*, m. p. 139° (*picrate*, m. p. 222°; *phenylthiosemicarbazide*, m. p. 225°), from p-*hydroxybenzaldazine*, m. p. 232°; o-*aminobenzylidene-hydrazine*, m. p. 62° (*dipicrate*, m. p. 188°), from *o*-aminobenzaldazine; m-*methoxybenzylidenehydrazine*, b. p. 174—175°/21 mm. (*phenylthio-semicarbazide*, m. p. 153°), from *m*-methoxybenzaldazine; *p*-methoxy- and *p*-ethoxy-benzaldazines yield the corresponding benzylidenehydrazines, which, however, revert to the original benzaldazines during the process of isolation by ether. *Heptylidenehydrazine*,

$$CH_3\cdot[CH_2]_5\cdot CH\colon N\cdot NH_2,$$

b. p. 164—165°/12 mm., was prepared from heptaldehyde and aqueous hydrazine hydrate.

The water formed during the production of mixed aldazines by the condensation of benzylidenehydrazines and aldehydes complicates the reaction by attacking the benzylidenehydrazine, whereby a second aldazine is formed and hydrazine hydrate, which then reacts with the aldehyde to produce a third aldazine. The authors prevent the by-reactions by using, instead of the aldehyde, its condensation product with aniline; thus, benzylidenehydrazine and ethereal *m*-nitrobenzyl-ideneaniline yield *s*-*m*-nitrodibenzylidenehydrazine; *m*-hydroxybenzyl-ideneaniline and ethereal benzylidenehydrazine yield m-*hydroxydibenzyl-idenehydrazine*, m. p. 162°; *p*-hydroxybenzylidenehydrazine and benzyl-ideneaniline yield p-*hydroxydibenzylidenehydrazine*, m p. 239—240°.

C. S.

Additive Compounds of Aromatic Amines with Phenols. JOSEF DOLLINGER (*Monatsh.*, 1910, **31**, 643—656. Compare Dyson, Trans., 1883, **43**, 466; Hebebrand, Abstr., 1883, 61; Philip, Trans., 1903, **83**, 814; Philip and Smith, *ibid.*, 1905, **87**, 1735; Kremann, Abstr., 1906, ii, 266; Schreinemakers, Abstr., 1899, ii, 739; 1900, ii,

135).—Additive compounds of quinol, α- and β-naphthol with benzidine, o-tolidine, and o-dianisidine can be prepared by mixing together hot saturated aqueous solutions of the components. They are all practically insoluble in water, are resolved into their components when boiled with dilute acids or alkalis, and with the exception of the compound of o-tolidine and α-naphthol, contain an equal number of hydroxyl and amino-groups. Most of the compounds give characteristic colorations with ferric chloride in aqueous solution.

The *additive compound* of benzidine and quinol,

$$C_{12}H_8(NH_2)_2,C_6H_4(OH)_2,$$

is best prepared from cold alcoholic solutions, and forms colourless, glistening, rhombic plates, m p. 230° (decomp.). The *additive compound* of benzidine and β-naphthol, $C_{12}H_8(NH_2)_2,2C_{10}H_7{\cdot}OH$, forms colourless, iridescent plates, m. p. 177°.

The amount of quinol or β-naphthol in an aqueous solution can be determined by adding benzidine solution and weighing the product (97% of the theoretical). The *additive compound* of o-tolidine and quinol, $C_{12}H_6Me_2(NH_2)_2,C_6H_4(OH)_2$, can be prepared from ethereal solutions, and forms microscopic needles with a red colour. It has m. p. 158° after sintering at 140°. The *additive compound* of o-tolidine and α-naphthol, $C_{12}H_6Me_2(NH_2)_2,C_{10}H_7{\cdot}OH$, crystallises from dilute alcohol in reddish-coloured needles, m. p. 99°. The *additive compound* of o-tolidine and β-naphthol,

$$C_{12}H_6Me_2(NH_2)_2,2C_{10}H_7{\cdot}OH,$$

crystallises in glistening plates, m. p. 96°. The *additive compound* of dianisidine and quinol, $C_{12}H_6(OMe)_2(NH_2)_2,C_6H_4(OH)_2$, separates from a mixture of benzene and light petroleum as pale lilac-coloured crystals, m. p. 157° (decomp.). The *additive compound* of dianisidine and β-naphthol, $C_{12}H_6(OMe)_2(NH_2)_2,2C_{10}H_7{\cdot}OH$, crystallises in long, reddish-coloured needles, m. p. 96°. The *additive compound* of α-naphthylamine and α-naphthol, $C_{10}H_7{\cdot}NH_2,C_{10}H_7{\cdot}OH$, forms pale lilac-coloured needles, m. p. 60°, and is decomposed by boiling water. The *additive compound* of α-naphthylamine and β-naphthol crystallises in glistening, rose-coloured prisms, m. p. 73—74°. The *additive compound* of β-naphthylamine and β-naphthol forms colourless prisms, m. p. 125—126°.

The following pairs of substances do not form sparingly soluble additive compounds: β-Naphthylamine and α-naphthol, α-naphthylamine and quinol, benzidine and catechol, benzidine and resorcinol.

Some of the compounds appear to be acidic, others basic, and still others amphoteric. J. J. S.

Preparation of Condensation Products in the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 222205).—The condensation of aminoanthraquinones with halogen ketones yielding products of the type A·NH·R·CO·R·NH·A has been previously described (this vol., i, 397); the reaction has now been extended to halogen diketones of the general type H·R·CO·CO·R·H (H = halogen), which yield with aminoanthraquinones a new series of compounds of the general formula A·NH·R·CO·CO·R·NH·A (A = anthraquinone residue).

4 : 4′-Dichlorobenzil (50 parts) is boiled with 1-aminoanthraquinone (100 parts) and sodium carbonate (20 parts) in nitrobenzene solution in the presence of cupric oxide until the reaction is complete, when, on cooling, the product separates in brown needles. The nitrobenzene can be replaced by other indifferent solvents, and the copper oxide by cuprous chloride. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 222206).—An extension of the type of condensation described in the previous patent; in the present case the general reaction is that by which one or more anthraquinone residues are connected through an imino-group with one or more phenanthraquinone radicles. Two mols. of a mono-halogenated phenanthraquinone may condense with 2 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone; similarly, one molecular proportion of a dihalogenated phenanthraquinone may combine with 2 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone. These condensations take place in boiling nitrobenzene solution in the presence of copper oxide and sodium carbonate or acetate.

The *product* from monobromophenanthraquinone (3 parts) and 1-aminoanthraquinone (2·4 parts) is a violet-brown powder, insoluble in water, alkali, and dilute acids; it yields a violet-brown colour with concentrated sulphuric acid, and violet-brown with boric acid.

The *products* from monobromophenanthraquinone (4·8 parts) and 1 : 5-diaminoanthraquinone (2 parts), from dibromophenanthraquinone (5 parts) and 1-aminoanthraquinone (10 parts), and from dichlorophenanthraquinone (3 parts) and 1-aminoanthraquinone (3 parts) were also prepared.

The *dibromophenanthraquinone* was obtained by brominating phenanthraquinone in nitrobenzene solution at 100°, the product separating in crystalline form from the hot solution; it crystallises from acetic acid in long, glistening, golden needles, m. p. 388°.

Dichlorophenanthraquinone was analogously prepared in the presence of a halogen carrier; it crystallises from acetic acid in red needles, m. p. above 300°. F. M. G. M.

Tetramethylchrysaniline. OTTO FISCHER and EDG. SCHMIDT (*J. pr. chem.*, 1910, [ii], **82**, 288—291).—The by-product obtained when 2-aminotetramethyl-4′ : 4″-diaminotriphenylmethane is oxidised by arsenic acid (Abstr., 1882, 833) is produced in larger quantity when a boiling solution of the leuco-base in xylene is treated with yellow mercuric oxide for twelve to fifteen hours. The suggestion that it is tetramethylchrysaniline, m. p. 229—230°, is proved to be correct. The *platinichloride* and *picrate* are described; the *nitrate*,

$$C_{23}H_{23}N_3,HNO_3,$$

is readily soluble in water. C. S.

Preparation of Azoxy-compounds. FRITZ REITZENSTEIN (*J. pr. Chem.*, 1910, [ii], **82**, 252—270).—By the oxidation of certain aromatic mono- or di-amines by warm alkaline potassium ferricyanide, the author has obtained dyes which he regards as containing the azoxy-

group. The dyes are produced in satisfactory yield, are substantive in character, and generally can be diazotised and combined on the fibre. After the removal of the dye, chlorine is passed into the mother liquor, which can then be utilised again; thus dianisidine gives the *substance*,

$$OMe\cdot C_6H_3(NH_2)\cdot C_6H_3(OMe)\cdot \underset{\diagdown O \diagup}{N-N}\cdot C_6H_3(OMe)\cdot C_6H_3(OMe)\cdot NH_2,$$

a dark red powder, which dyes wool and silk yellow. Aniline-*p*-sulphonic acid yields the *substance*, $SO_3Na\cdot C_6H_4\cdot \underset{\diagdown O \diagup}{N-N}\cdot C_6H_4\cdot SO_3Na$, and 2 : 6-dibromoaniline-4-sulphonic acid a corresponding *substance*, which is brick-red and dyes wool a more intense yellow than the preceding substance. Similar azoxy-dyes are produced from benzidinesulphonedisulphonic acid, benzidinesulphonic acid, naphthidine, *oo'*-diaminodiphenic acid, *p*-phenylenediaminesulphonic acid, atoxyl (*p*-aminophenylarsinic acid), diaminostilbenedisulphonic acid, diaminotolan, and 4 : 4'-diaminodiphenylmethane. C. S.

***endo*Bisazo-derivatives of Diphenylmethane.** HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 852—861. Compare this vol., i, 559, 588).—The general character of this investigation has been discussed already, and most of the results recorded (Abstr., 1907, i, 663; 1908, i, 658, 706). The following new compounds are described: Bisazodiphenylmethane-4 : 4-dicarboxylic acid (*loc. cit.*) on reduction with zinc and hydrochloric acid furnishes *bishydrazodiphenylmethane*-4 : 4'-*dicarboxylic acid*, which is amorphous, but yields a *tetracetyl* derivative, crystallising in small, yellow needles. T. A. H.

Hemielastin. ELKAN WECHSLER (*Zeitsch. physiol. Chem.*, 1910, 67, 486—488).—Hemielastin (Horbaczewski, Abstr., 1883, 927) when hydrolysed with sulphuric acid gave the following numbers: ammonia, 0·4; humin nitrogen I, 3·1; humin nitrogen II, 4·9; histidine, 1·0; arginine, 4·2; monoamino-acids, 71·1; lysine, 3·4% of the total nitrogen.

These correspond with arginine, 1·86; histidine, 0·53; lysine, 2·48, and ammonia, 0·05% of the original hemielastin. J. J. S.

Guanylic Acid from the Pancreas. II. HERMANN STEUDEL and P. BRIGL (*Zeitsch. physiol. Chem.*, 1910, 68, 40—51. Compare Steudel, Abstr., 1908, i, 70)—Bang's β-guanylic acid is regarded as the acid potassium salt of guanylic acid. When repeatedly dissolved in water and precipitated, it becomes more soluble, owing to loss of potassium. The formula suggested is $C_{10}H_{13}O_8N_5PK$. A corresponding barium salt has been prepared. The amounts of guanine and pentose formed on hydrolysis agree with the amounts required for such a formula.

The pentose is shown to be arabinose.

Levene's guanosine could not be isolated (compare Abstr., 1909, i, 620). J. J. S.

Non-existence of Free or Combined Lecithins in the Yolk of Eggs. N. ALBERTO BARBIERI (*Compt. rend.*, 1910, **151**, 405—407. Compare Abstr., 1907, ii, 708).—From experiments on the yolks of 3000 eggs, the author has been unable to obtain any evidence for the existence of lecithins in this material. The fatty matters can be separated in a state of purity by the aid of neutral solvents. They contain nitrogenous substances, but these can be removed by simple dialysis, and chlorine was not detected amongst them. The fats yield on hydrolysis nothing but glycerol and fatty acids. The phosphorus, moreover, was entirely dialysable, and appears to be present chiefly in the form of phosphates.

The portion of the yolk soluble in ether, commonly described as consisting of lecithins, yielded only small quantities of a *platinichloride*, m. p. 215°, containing 4·43% of nitrogen. The same salt was obtained from those constituents of the yolk soluble in water and alcohol.

W. O. W.

Iodoproteins. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, **27**, 261—270).—The author gives an account of some attempts to prepare iodine-containing hydrolysis products from iodoproteins, using iodogliadin, a derivative of wheat proteins. The method attempted was to partly hydrolyse the iodoprotein with sulphuric acid at about 37°, and then to digest the hydrolysis mixture with pancreatin, and to separate the iodo-derivative by fractionating out on copper. He also gives an account of similar experiments carried out by L. Scott on iodospongin. He draws attention to an error in the estimation of iodine in organic compounds when nitrate is employed in the destruction of organic matter, and water vapour is then distilled through the iodine-containing mixture in the presence of ferric chloride into potassium iodide solution. If nitrate is employed, nitric oxide, free chlorine (from the aqua regia), etc., interfere with the reaction.

S. B. S.

Gelatin and Tannin. HANS TRUNKEL (*Biochem. Zeitsch.*, 1910, **26**, 458—492).—Gelatin and tannin can be precipitated quantitatively from solution. The same quantity of lime (1 gram) requires more tannin for precipitation (0·7 gram) when fresh than when the solution has stood for twenty-four hours (0·4 gram). By warming the solution, however, the original proportions are re-attained. By this means a calcium tannate stable to water is obtained. If excess of tannin is employed, a precipitate is obtained from which tannin can be continually extracted by water. Neither the water-stable nor water-unstable precipitates can be separated into the components by alcohol, which extracts only 97% alcohol. From the gelatin residue only 6% of a gelatinising residue can be obtained. By treatment of both tannates with water or alcohol, a small amount of gallic acid is formed. The author shows that the quantitative relationships between the gelatin and tannin in the precipitates formed in various dilutions follow approximately the exponential adsorption equation, and he concludes that chemical processes play but a subordinate part in the reaction between the two substances. S. B. S.

Organic Chemistry.

Relation between the Specific Gravity and Optical Constants of Isomeric Organic Compounds. K. HEYDRICH (*Zeitsch. Kryst. Min.*, 1910, **48**, 243—305).—The crystallographic constants, specific gravity, and refractive indices were determined for the following: Methyl oxalate (monoclinic, $a:b:c=1\cdot0351:1:0\cdot3346$; $\beta=101°55'$. D 1·422. Refractive indices for *D* line [values for *C* and *F* lines are also given for each of the compounds], $\alpha=1\cdot4177$, $\beta=1\cdot4616$, $\gamma=1\cdot5521$). Succinic acid (monoclinic, $a:b:c=0\cdot5688:1:0\cdot6195$; $\beta=91°20'$. D 1·562—1·567. $\alpha=1\cdot4503$, $\beta=1\cdot5338$, $\gamma=1\cdot6100$). Catechol (monoclinic, $a:b:c=1\cdot6086:1:1\cdot0229$; $\beta=94°15'$. D 1·367—1·375. $\alpha=1\cdot595$, $\beta=1\cdot609$, $\gamma=1\cdot747$). Resorcinol (orthorhombic, $a:b:c=0\cdot9110:1:0\cdot549$. D 1·281—1·285. $\alpha=1\cdot5781$, $\beta=1\cdot6197$, $\gamma=1\cdot6273$). Quinol (ditrigonal-scalenohedral, $a:c=1:0\cdot6680$. D 1·328—1·332. $\omega=1\cdot6325$, $\epsilon=1\cdot6262$). 2:4-Dinitrotoluene (monoclinic, $a:b:c=0\cdot85930:1:0\cdot54076$; $\beta=94°18'$. D 1·518—1·521. $\alpha=1\cdot4423$, $\beta=1\cdot6619$, $\gamma=1\cdot7556$). 2:6-Dinitrotoluene (orthorhombic, $a:b:c=0\cdot5714:1:0\cdot5407$. D 1·538—1·540. $\alpha=1\cdot4788$, $\beta=1\cdot6694$, $\gamma=1\cdot7244$). Codeine (orthorhombic, $a:b:c=0\cdot9595:1:0\cdot8346$. D 1·309—1·315. $\alpha=1\cdot5428$, $\beta=1\cdot6355$, $\gamma=1\cdot6838$). *iso*Codeine (orthorhombic, $a:b:c=0\cdot6322:1:0\cdot5600$. D 1·361—1·367. $\alpha=1\cdot6070$, $\beta=1\cdot6422$, $\gamma=1\cdot6754$). ψ-Codeine (monoclinic, $a:b:c=2\cdot1942:1:1\cdot1036$; $\beta=108°14'$. D 1·288—1·290. $\alpha=1\cdot5743$, $\beta=1\cdot6021$, $\gamma=1\cdot6472$). Dicyanodiamide (monoclinic,

$$a:b:c=1\cdot1109:1:1\cdot4213;\ \beta=115°20'.$$

D 1·404—1·405. $\alpha=1\cdot5212$, $\beta=1\cdot5493$, $\gamma=1\cdot8471$). Melamine (monoclinic, $a:b:c=1\cdot4121:1:0\cdot9728$; $\beta=112°16'$. D 1·573. $\alpha=1\cdot4906$, $\beta=1\cdot7429$, $\gamma=1\cdot8721$). Potassium phenol-*o*-sulphonate (orthorhombic, $a:b:c=0\cdot7796:1:0\cdot4621$. D 1·733—1·734. $\alpha=1\cdot5265$, $\beta=1\cdot5677$, $\gamma=1\cdot6467$). Potassium phenol-*p*-sulphonate (orthorhombic, $a:b:c=0\cdot8790:1:1\cdot0017$. D 1·869—1·871. $\alpha=1\cdot5714$, $\beta=1\cdot6079$, $\gamma=1\cdot6942$).

In each of these isomeric groups an increase in sp. gr. is accompanied by an increase in the mean refractive index, the specific refractive power remaining practically the same. For the polymeric substances there is a much greater difference in the specific refractive power. L. J. S.

Hydrocarbons of the Wool Grease Oleins. I. AUGUSTUS H. GILL and LAURENCE R. FORREST (*J. Amer. Chem. Soc.*, 1910, **32**, 1071—1073).—The hydrocarbons obtained by the hydrolysis of distilled wool grease oleins were freed from cholesterol and fractionally distilled under 1 mm. pressure. Each fraction was crystallised from acetone, so that the material was finally divided into two series of ethylenic hydrocarbons; the first, containing twelve terms soluble in acetone at 0°, ranged from heptadecylene to triacontylene, $C_{30}H_{60}$, whilst the insoluble series included nine members, from eicosylene,

$C_{20}H_{40}$, to nonacosylene, $C_{29}H_{58}$. The b. p., molecular weight, and iodine number of each fraction is given. W. O. W.

Historical Notes on *C*-Nitroso-compounds. EUGEN BAMBERGER (*Ber.*, 1910, **43**, 2353—2355. Compare Abstr., 1900, i, 500).—The following arguments are brought forward against Piloty's formula, CMe_2:NO·O·NO, for ψ-nitroles (*Ber.*, 1902, **35**, 3094 note).

(1) In all cases in which the hydrogen atom of the :NO·OH group of nitronic acid is replaced, the substituent becomes attached to carbon, for example, CHMe:NO·OH gives CH_3·CHBr·NO_2. (2) A nitrite of the type CMe_2:NO·O·NO, should be readily hydrolysed by water; ψ-nitroles are not. (3) Piloty's formula does not account in any way for the similarity between ψ-nitroles and true *C*-nitroso-compounds. J. J. S.

Action of Grignard's Reagents on Methylethylacraldehyde and the Preparation of Certain Diolefines. E. BJELOUSS (*Ber.*, 1910, **43**, 2330—2333).—A series of unsaturated secondary alcohols has been prepared by the action of magnesium ethyl, *iso*butyl, and *iso*amyl bromides on methylethylacraldehyde, and these alcohols have been transformed into diolefines containing conjugate double linkings by means of crystallised oxalic acid (Zelinsky, Abstr., 1902, i, 2).

δ-Methyl-Δ^γ-hepten-ε-ol, CHEt:CMe·CHEt·OH, prepared from ethyl magnesium bromide and methylethylacraldehyde, is a colourless liquid with a strong odour, and has b. p. 103—104°/75 mm., D_4^{25} 0·8545, and n_D^{25} 1·44436. The *acetate*, $C_{10}H_{18}O_2$, has b. p. 113°/80 mm., and the *chloride*, $C_8H_{15}Cl$, b. p. 75—78°/53 mm. *δη-Dimethyl-Δ^γ-octen-ε-ol*, CHEt:CMe·CH(OH)·CH_2·$CHMe_2$, is a colourless, mobile liquid, b. p. 108—111°/40 mm. It has D_4^{25} 0·8444 and n_D^{25} 1·44503. The *acetate*, $C_{12}H_{22}O_2$, has b. p. 103—105°/20 mm., and the *chloride*, $C_{10}H_{19}Cl$, b. p. 76—79°/13 mm.

δθ-Dimethyl-Δ^γ-nonen-ε-ol, CHEt:CMe·CH(OH)·CH_2·CH_2·$CHMe_2$, has b. p. 110—112°/19 mm., D_4^{25} 0·8441, and n_D^{25} 1·44782. The *acetate*, $C_{13}H_{24}O_2$, has b. p. 122—125°/31 mm., and the *chloride*, $C_{11}H_{21}Cl$, b. p. 93—95°/18 mm., but evolves hydrogen chloride.

δ-Methyl-Δ^{βδ}-heptadiene, CHEt:CMe·CH:CHMe, is a colourless, mobile liquid, b. p. 131—132°. It has D_4^{25} 0·7551 and n_D^{25} 1·46211, and shows the usual exaltation.

βε-Dimethyl-Δ^{γε}-octadiene, CHEt:CMe·CH:CH·$CHMe_2$, has b. p. 165°, D_4^{25} 0·7754, and n_D^{25} 1·46136.

δθ-Dimethyl-Δ^{γε}-nonadiene, CHEt:CMe·CH:CH·CH_2·$CHMe_2$, has b. p. 185—189°, D_4^{25} 0·7779, and n_D^{25} 1·46189. J. J. S.

Preparation of Keto-alcohols. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 223207).—The condensation products of ketones and alcohols have previously been described (compare Abstr., 1905, i, 443, 732); when this reaction is carried out in the presence of alkali carbonates or hydroxides, it yields stable compounds of therapeutic value.

Methyl hydroxyethyl ketone, CH_3·CO·CH_2·CH_2·OH, a colourless,

odourless oil, miscible with water, alcohol, or ether in all proportions, b. p. 109—110°/30 mm., is prepared by treating acetone (3 parts) with 35% formaldehyde solution (1 part), slowly adding potassium carbonate, heating to 30—35°, and subsequently distilling the acidified solution in a vacuum. The *acetate* is a colourless oil, b. p. 96°/15 mm.

*Methyl β-hydroxy*iso*propyl ketone*, $CH_3\cdot CO\cdot CHMe\cdot CH_2\cdot OH$, a viscous, colourless oil, b. p. 90—95°/15 mm., is prepared in similar manner from methyl ethyl ketone. F. M. G. M.

The Fatty Acids. S. FACHINI and G. DORTA (*Boll. chim. farm.*, 1910, **49**, 237—247).—The authors base a method for the separation of the solid fatty acids from the liquid and unsaturated fatty acids on the sparing solubility of the former in light petroleum of low boiling point (30—50°). Solutions of stearic, palmitic, and myristic acids in this solvent deposit the whole of the dissolved substance when cooled to −40° in alcohol and solid carbon dioxide. Lauric acid is somewhat more soluble. The separation of the above acids on cooling is also almost quantitative even when the solution contains liquid fatty acids. It cases where large amounts of the former are present in the mixture, it is advisable first to remove the greater part of them from the solution by moderate cooling, and subsequently to precipitate the rest at −40°. This procedure facilitates filtration. The method is conveniently employed for the separation of arachidic acid, which crystallises along with lignoceric acid when the fatty acids from arachis oil are treated in the manner indicated. R. V. S.

Mixed Anhydrides. ENOS FERRARIO (*Gazzetta*, 1910, **40**, ii, 95—100).—The method of preparation of benzoyl nitrate by the action of benzoyl chloride and silver nitrate (Francis, Trans., 1906, **89**, 1) may be applied to other organic nitrates, and also to nitrites.

Acetyl nitrite, $CH_3\cdot CO\cdot NO_2$, is prepared by the action of acetyl chloride on dry silver nitrite at −30° to −40°. It is finally distilled at 45° in carbon dioxide. For the purpose of estimating the nitrogen, the vapours are passed, mixed with carbon dioxide, over a heated copper spiral. Propionyl, butyryl, and benzoyl nitrites are prepared in similar manner. The nitrites obtained are identical with those prepared by Francesconi and Cialdea (Abstr., 1904, i, 707) by the action of nitrosyl chloride on silver salts. C. H. D.

Preparation of Derivatives of ββ-Dialkylpropionic Acids. FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 222809).—It is found that the derivatives of ββ-dialkylpropionic acids of the general formula $CHR_1R_2\cdot CH_2\cdot CO_2H$ (where R_1 and R_2 are alkyl radicles) have with the exception of the methyl and ethyl derivatives valuable therapeutic properties, and are quite tasteless.

β-Ethylvaleryl chloride, b. p. 150—155°, prepared from β-ethylvaleric acid and phosphorus pentachloride, yields when treated with ammonium hydroxide, *β-ethylvalerylamide*, m. p. 127·5°; the *carbamide*, m. p. 197°, is prepared in the usual manner.

Menthyl β-ethylvalerate, b. p. 155°/12 mm., is obtained by the action of the foregoing chloride on menthol in the presence of pyridine.

F. M. G. M.

Glucinum Lactate. G. CALCAGNI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 229—233, 290—293).—From glucinum carbonate and lactic acid a salt of the composition $Gl_{13}(C_3H_5O_3)_6O_{10},19H_2O$ can be obtained, but it is not a chemical individual, for when its aqueous solution is fractionally precipitated with alcohol, precipitates of various compositions are obtained. Indirectly, however, indications were obtained of the existence of salts of compositions other than those studied by previous authors. The specific conductivity of a solution of lactic acid to which glucinum oxide is added at first decreases, then increases rapidly until one half the molecular quantity of the oxide is present. The conductivity then rises, but very slightly, reaching a maximum when the molecular quantity of glucinum oxide has been added. Further addition of glucinum oxide causes a decrease in conductivity. These results are obtained at all degrees of dilution, and analogous behaviour is observed when the depression of the freezing point of the solution is measured. Hence it is probable that in addition to the normal salt which has been supposed to exist, another is formed composed of equimolecular quantities of base and acid. Above the concentration corresponding with this salt, glucinum oxide dissolves in the solution without forming salts, and its presence modifies the nature of the solvent, so that the conductivity and freezing point of the solvent are lowered (compare Parsons, Robinson, and Fuller, Abstr., 1908, ii, 105). R. V. S.

Action of Sodium Alkyloxides on Ethyl Acetoacetate. TELEMACHOS KOMNENOS (*Monatsh.*, 1910, **31**, 687—693. Compare this vol., i, 361).—By the interaction of sodium methoxide and ethyl acetoacetate in methyl-alcoholic solution a practically quantitative yield of methyl acetoacetate can be obtained. When sodium amyloxide and amyl alcohol are used, amyl acetoacetate is obtained. The formation of ethyl acetoacetate from sodium ethoxide and methyl acetoacetate in ethyl-alcoholic solution also takes place readily.

In the distillation of methyl acetoacetate there is no formation of dehydracetic acid, but the latter is formed in large quantity when amyl acetoacetate is distilled, and the author recommends this as the best method of preparation. T. S. P.

Ozo-salts of Molybdenum. ARRIGO MAZZUCCHELLI and G. ZANGRILLI (*Gazzetta*, 1910, **40**, ii, 49—73).—It has been shown (Abstr., 1907, i, 748) that molybdenum peroxide is capable of forming a complex oxalate. A number of similar salts have now been examined.

The addition of hydrogen peroxide to a solution of ammonium molybdenum oxalate yields a yellow solution, which deposits crystals of a *salt*, $(NH_4)_2C_2O_4,MoO_4$. When dilute solutions are used, a product containing a smaller proportion of oxygen is obtained. The *potassium* salt, $K_2C_2O_4,MoO_4$, forms yellow crystals. If finely powdered and shaken with hydrogen peroxide, crystals of a *salt*,

$$K_2C_2O_4,2MoO_4,3H_2O,$$

separate, and an orange *ammonium* salt of corresponding composition has been obtained. The sodium salt, precipitated by alcohol, has the

composition $Na_2C_2O_4,Mo_2O_7$, probably owing to hydrolysis. Potassium molybdoiodate yields only an amorphous product on oxidation, and ammonium molybdophosphate yields a product which does not contain active oxygen.

Potassium molybdoarsenate and hydrogen peroxide yield only a potassium ozomolybdate, $K_2MoO_5,3H_2O$, free from arsenic.

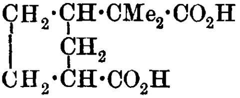
Cryoscopic measurements have been made, using solutions of various complex salts and acids of molybdenum, and adding successive quantities of hydrogen peroxide. The results show that the number of molecules present in the solution is not increased by such additions until the ratio $H_2O_2 : MoO_3$ is reached, and it appears that even a further quantity enters into combination. Such a salt as $(NH_4)_2C_2O_4,MoO_5$ may exist, the salt KVO_5 being already known.

The results are, however, complicated by a decomposition of the complex salts, and do not admit of any simple interpretation. Measurements with methyl molybdate have also been made as a means of determining the molecular complexity. C. H. D.

Synthesis of the αδ-Dimethyladipic Acids and Separation of the Racemic Acid into Optical Isomerides. William A. Noyes and L. P. Kyriakides (*J. Amer. Chem. Soc.*, 1910, **32**, 1057—1061).—Lean has expressed the view that the carbon atoms in αβ-dialkylsuccinic acids and similar compounds are so united that optical isomerism is impossible (Trans., 1894, **65**, 1001). That this is not the case is now shown by the resolution of αδ-dimethyladipic acid through the agency of its acid brucine salts. d-*αδ-Dimethyladipic acid*, m. p. 104—105°, has $[\alpha]_D^{28} + 31{\cdot}3°$ in 10% alcoholic solution. The *l*-form was obtained in an impure condition, having $[\alpha]_D - 23{\cdot}4°$. Attempts to resolve the meso-form were unsuccessful.

The preparation of αδ-dimethyladipic acid is considerably facilitated by substituting magnesium amalgam (Meunier, Abstr., 1904, i, 7) for sodium in the condensation of ethylene dibromide with ethyl malonate. W. O. W.

Camphenic (Camphenecamphoric) Acid. Ossian Aschan (*Annalen*, 1910, **375**, 336—378).—Camphenic acid (the name is proposed by the author for camphenecamphoric acid) constitutes about 70% of the total oxidation products of camphene, whether natural or artificial, by alkaline potassium permanganate. In support of the annexed formula, the following facts are stated.



Camphenic acid, $C_8H_{14}(CO_2H)_2$, m. p. 135·5—136·5°, is a saturated, monocyclic dicarboxylic acid which does not form an anhydride. It is a racemic compound, the active forms being optical antipodes, $[\alpha]_D \pm 1{\cdot}8°$, m. p. 143—144°; the *l*-form has been obtained by Wallach and Gutmann (Abstr., 1907, i, 1061), and the *d*-form by the author by the oxidation of a highly dextrorotatory camphene prepared from Grecian turpentine. Like camphoric acid, camphenic acid is converted by glacial acetic acid and hydrochloric acid, D 1·2, at 180° into an *isomeride* (trans-form ?), which, however, could not be isolated in a pure state (the separation of the two isomeric

acids has since been accomplished by Wallach). Camphenic acid (1 mol.) is treated with phosphorus pentachloride (2 mols.), and, after the cessation of the reaction, with bromine (rather more than 1 mol.) in the cold, whereby under conditions detailed by the author *a-bromocamphenic acid*, $C_8H_{15}Br(CO_2H)_2$, m. p. 190°, is obtained; only 1 atom of the halogen can be introduced smoothly. When bromocamphenic acid is heated with a solution of sodium carbonate on the water-bath for about fifteen minutes, it is partly converted into *dehydrocamphenic acid*, m. p. 155°, which receives the constitution $CO_2H\cdot CMe_2\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ CH:C\cdot CO_2H\end{array}$, because it is converted by nitric acid, D 1·252, on the water-bath into the *γ-lactone*,

$$CO_2H\cdot CMe_2\cdot C(CO_2H)<\begin{array}{l}CH_2\cdot CH_2\\ O\text{---}CO\end{array},$$

m. p. 254° (decomp.). The decomposition of the lactone by fusion with potassium hydroxide yields chiefly *iso*butyric acid, together with succinic and oxalic acids. The action of sodium carbonate on bromocamphenic acid also results in the formation of *hydroxycamphenic acid*,

$$CO_2H\cdot CMe_2\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot C(OH)\cdot CO_2H\end{array},$$

m. p. 152°, which is stable to potassium permanganate, and is not affected by 40% sulphuric acid on the water-bath, thus proving that the hydroxyl group is not in the γ-position to a carboxyl group.

Whilst bringing forward the preceding constitution of camphenic acid with reserve, the author claims that much can be said in favour of the annexed constitution of camphene. Touching on the vexed question of the nature of camphene, the author is disinclined to accept Moycho and Zienkowski's suggestion of its dual character (Abstr., 1904, i, 438; 1905, i, 710), but leans to Semmler's view of its homogeneity. Nevertheless, in consequence of the large percentage of camphenic acid obtained by the oxidation of camphene, he rejects Wagner's "methylene" formula of camphene (which necessitates the assumption of the formation of several intermediate substances in order to explain the formation of camphenic acid) and proposes the "ethylene" formula given above. Certainly Wagner's claim that the camphenic acid is produced from the intermediately formed camphenylic acid must be wrong, because, as the author shows, the latter does not yield camphenic acid when oxidised by potassium permanganate. The formation of camphenic and camphenylic acids by the oxidation of camphene by alkaline potassium permanganate is easily explicable by the author's formula:

$$\begin{array}{lll}CH_2\cdot CH\text{--}CMe_2\\ \vert \qquad \vert \qquad \vert\\ \vert \quad CH_2 \quad CH\\ \vert \qquad \vert \qquad \Vert\\ CH_2\cdot CH\text{--}CH\end{array}$$

$$C_8H_{14}<\begin{array}{l}CH\\ \Vert\\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot OH\\ \vert\\ CH\cdot OH\end{array} \longrightarrow$$

$$C_8H_{14}<\begin{array}{l}CO\\ \vert\\ CO\end{array}\begin{array}{l}\longrightarrow C_8H_{14}(CO_2H)_2\\ \longrightarrow C_8H_{14}:C(OH)\cdot CO_2H\end{array}$$

the camphenylic acid being produced by a "benzylic acid" transformation in manner quite analogous to the formation of β-fenchocarboxylic acid from carbofenchenone. C. S.

New Formation of Carboxylic Acids of the Carbohydrates. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, **28**, 355—358).—By the oxidation of dextrose with nitric acid (D 1·15) in addition to saccharic acid, a *carboxylic acid*, $CHO\cdot[CH\cdot OH]_4\cdot CO_2H$, identical or isomeric with glycuronic acid is formed. The *barium* salt, a colourless powder, and the free acid both strongly reduce Fehling's solution, give an intense colour reaction with naphtharesorcinol, and also show positive phloroglucinol and orcinol tests. Barium hydroxide produces a precipitate of an orange-coloured, flocculent basic salt. A furfuraldehyde distillation showed the conversion of 10 per cent. of the original dextrose into this form. E. F. A.

Carbithionic Acids. IV. Esters of Perthio-acetic, -propionic, and -phenylacetic Acids. JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1910, **43**, 2481—2485. Compare Abstr., 1907, i, 382, 474).—*Methyl dithioacetate*, $CH_3\cdot CS\cdot SMe$, is prepared by the interaction of magnesium methyl iodide with carbon disulphide, treatment of the reaction mixture with ice, followed by the addition of ammonium chloride. The carbithionate is shaken with methyl sulphate, when a red oil separates, which is distilled with steam to destroy excess of methyl sulphate. The ester is a reddish-yellow oil, b. p. 80—81°/95 mm., 71°/70 mm., 142°/760 mm., D_4^{21} 1·096; it has a characteristic odour.

Methyl dithiopropionate, $CH_2Me\cdot CS\cdot SMe$, is a reddish-yellow oil, b. p. 92—93°/70 mm., 47°/11 mm., 159—160°/760 mm., D_4^{21} 1·047.

Methyl dithiophenylacetate, $CH_2Ph\cdot CS\cdot SMe$, is a reddish-yellow oil of characteristic odour, b. p. 149°/12 mm., 280°/760 mm. (decomp.), D_4^{24} 1·1389. E. F. A.

Hyposulphites. VIII. Aldehydesulphoxylates and Potassium Cyanide. ARTHUR BINZ and TH. MARX (*Ber.*, 1910, **43**, 2350—2352. Compare Binz, Abstr., 1909, ii, 229).—Neither rongalite nor potassium cyanide alone reduces indigocarmin in the cold, whereas a mixture of the two does. It is also shown that potassium cyanide accelerates the reducing power of rongalite towards indican, whereas it has no such effect on benzaldehydesulphoxylate.

The effects are probably catalytic. The reaction with indigocarmin is of interest, as it belongs to the group of reactions which take place only after the lapse of a certain time. J. J. S.

Dissociation Processes in the Sugar Group. II. Behaviour of Carbohydrates towards Alkali Hydroxides. JOHN U. NEF (*Annalen*, 1910, **376**, 1—119. Compare Abstr., 1905, i, 3; 1908, i, 5). —Twenty-four isomeric saccharinic acids with six carbon atoms are possible, namely, eight stereoisomeric *meta*saccharinic acids ($\alpha\gamma\delta\epsilon$-tetrahydroxyhexoic acids), $CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, derived from the sixteen aldohexoses; four stereoisomeric *iso*saccharinic acids ($\alpha\gamma\delta$-trihydroxy-α-hydroxymethylvaleric acids),

$$CO_2H\cdot C(OH)[CH_2(OH)]\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

derived from the eight β-ketohexoses; eight saccharinic acids ($\alpha\beta\gamma\delta$-tetrahydroxy-α-methylvaleric acids),

$$CO_2H\cdot CMe(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH;$$

and four *para*saccharinic acids ($\alpha\beta\gamma$-trihydroxy-$\alpha(\omega)$-hydroxyethyl-

butyric acids), $OH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CO_2H) \cdot CH(OH) \cdot CH_2 \cdot OH$. The eight saccharinic acids are formed from the eight 3-ketohexoses, but the *para*saccharinic acids are not obtained by the action of alkali hydroxides. Hence the number of possible C_6 saccharinic acids derived from the thirty-two different hexoses is theoretically twenty isomerides.

In the case of all carbohydrates, whether aldoses or ketoses, and irrespective of the number of carbon atoms, the salt formation with alkali hydroxides takes place at the carbon atom next the carbonyl group, $-CH(OH) \cdot CH(OM) \cdot CO-$. The methylene derivative,

$$-CH(OH) \cdot \underset{\wedge}{C} \cdot CO-,$$

in the absence of an oxidising agent undergoes rearrangement to glycide,

$$\underset{\diagdown \; O \; \diagup}{-CH \cdot CH \cdot CO-}$$

, and this to *ortho*-osone, $-CH_2 \cdot CO \cdot CO-$, from which by the benzilic acid tranformation saccharinic acids are formed. In the presence of an oxidising agent, oxygen is absorbed, and the 1 : 2-osone, $-CH(OH) \cdot CO \cdot CO-$, is formed. Enzymes act in a similar manner on the carbohydrates, but their barely basic nature does not bring about the transformation of the *ortho*-osones formed into saccharinic acids.

Similarly, four C_4 saccharinic acids are derived from the six isomeric tetroses, and ten C_5 saccharinic acids from the fifteen isomeric pentoses; in the following the two $\alpha\gamma$-dihydroxybutyric acids, the four $\alpha\gamma\delta$-trihydroxyvaleric acids, and α- and β-dextro*meta*saccharinic acids are described.

Hexoses decompose into a molecule each of diose and aldotetrose, or into 2 molecules of glyceraldehyde; the decomposition into formaldehyde and an aldopentose has never been observed. In nature, pentoses are never formed by the degradation of hexoses; hexoses are never built up from pentoses and formaldehyde. Pentoses form $\alpha\beta$-dienols, $OH \cdot CH \colon C(OH) \cdot (CH \cdot OH)_2 \cdot CH_2 \cdot OH$, which in the main give aldotetroses and hydroxymethylene; to some slight extent they form $\beta\gamma$-dienols, $OH \cdot CH_2 \cdot C(OH) \colon C(OH) \cdot CH(OH) \cdot CH_2 \cdot OH$, which decompose into diose and glyceraldehyde. Dextroses exclusively form 2 : 3-dienols, and decompose into 2 molecules of diose; they never form hydroxymethylene and glyceraldehyde.

When hexoses or pentoses are treated with $8N$-sodium hydroxide, only the C_6 or C_5 saccharinic acids of the corresponding series are formed, as the products of decomposition (hydroxymethylene, diose, glyceraldehyde, and aldotetrose) do not under these conditions undergo synthetic condensation to every possible hexose and pentose. Hydroxymethylene, however, forms the dienol, $CH(OH) \colon CH(OH)$; this changes into glycolaldehyde, $CH_2(OH) \cdot CHO$, which condenses exclusively to tetrose, from which *d*- and *l*-$\alpha\gamma$-dihydroxybutyric acids are formed. It is not certain whether glyceraldehyde in the same manner gives exclusively *d*- and *l*-lactic acids.

When dilute sodium hydroxide is used, a mixture of every possible saccharinic acid with three, four, five, or six carbon atoms is obtained. This is the case when sparingly soluble metallic hydroxides, such as those of calcium and barium, are used. With $8N$-sodium hydroxide the

pentoses give only six saccharinic acids, and hexoses only eight, namely, *d*- and *l*-lactic acids, *d* and *l*-$\alpha\gamma$-dihydroxybutyric acids, and two *meta*- and two *iso*-saccharinic acids with six carbon atoms.

I. *l*-Arabinose and 8*N*-sodium hydroxide; 100 grams of sugar yield about 80 grams of non-volatile saccharinic acids, together with more or less of a dark reddish-brown, neutral resin soluble in water; this is chiefly formed from diose. After a lengthy process of separation, for the details of which the original must be consulted, d-*threo*-$\alpha\gamma\delta$-*trihydroxyvaleric acid*, $CO_2H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2\cdot OH$, and l-*erythro*-$\alpha\gamma\delta$-*trihydroxyvaleric acid*, $CO_2H-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2\cdot OH$, were isolated.

The *quinine* salt of the former crystallises in lustrous needles, m. p. 172°, $[\alpha]_D^{20}$ $-103\cdot3°$. The *phenylhydrazide* forms voluminous, colourless needles, m. p. 110°, $[\alpha]_D$ $+26\cdot36°$. The *brucine* salt separates in flat, lustrous prisms, $[\alpha]_D^{20}$ $-18\cdot77°$; the *sodium* salt has $[\alpha]_D^{20}$ $+23\cdot76°$.

d-*Threo*-$\alpha\delta$-*dihydroxyvalerolactone* is a colourless, mobile oil, $[\alpha]_D$ $-36\cdot5°$; it is oxidised by dilute nitric acid to d-$\alpha\gamma$-*dihydroxy-diglutaric acid*, m. p. 135°, $[\alpha]_D^{20}$ $-2\cdot6°$; the *disodium* salt has $[\alpha]_D^{20}$ $+22\cdot25°$.

l-*Erythrotrihydroxyvaleric acid* forms a *phenylhydrazide*, crystallising in colourless, concentrically-grouped, dense needles, m. p. 145—150°, $[\alpha]_D^{20}$ $-8\cdot93°$. The *lactone* has $[\alpha]_D^{20}$ $-45°$ to $-55°$.

dl-$\alpha\gamma$-*Dihydroxybutyric acid* forms a *brucine* salt, m. p. 188° (decomp.), $[\alpha]_D^{20}$ $-27\cdot23°$, and a *phenylhydrazide*, crystallising in needles, m. p. 130—131°; on oxidation, *dl*-malic acid is formed.

dl-$\beta\gamma$-*Dihydroxybutyric acid* yields a *phenylhydrazide*, m. p. 99°.

dl-$\alpha\gamma$-*Dihydroxybutyric acid* can be resolved by means of brucine. The *brucine* salt of the *d*-isomeride had m. p. 188° (decomp.), $[\alpha]_D^{20}$ $-20\cdot1°$, the free acid having $[\alpha]_D$ $+20°$ (about); it yields *d*-malic acid on oxidation.

II. Glycollaldehyde and strong sodium hydroxide form a good deal of resin and traces of formic acid, the main product being *dl*-α-hydroxybutyrolactone. No trace of *dl*-lactic acid is formed.

III. *l*-Xylose with 8*N*-sodium hydroxide yields *l*-threo- and *d*-ethryo-trihydroxyvaleric acids, the antipodes of those given by *l*-arabinose. The *quinine* salts of these two acids crystallise together, m. p. 165°, $[\alpha]_D$ $-113\cdot2°$; that of the d-*erythro*-$\alpha\gamma\delta$-*trihydroxyvaleric acid* forms lustrous needles, m. p. 172°, $[\alpha]_D$ $-104°$. The *phenylhydrazide* has m. p. 150°, $[\alpha]_D^{20}$ $+9\cdot38°$.

l-*Threo*-$\alpha\gamma\delta$-*trihydroxyvaleric acid* forms a *brucine* salt, crystallising in transparent, concentrically-grouped, flat prisms, m. p. 145—150°, $[\alpha]_D^{20}$ $-34\cdot07°$; a *quinine* salt, separating in needles, m. p. 160—162°, $[\alpha]_D^{20}$ $-119\cdot45°$; a *phenylhydrazide*, crystallising in colourless needles, m. p. 110—112°, $[\alpha]_D^{20}$ $-25\cdot43°$, and a *lactone*, $[\alpha]_D^{20}$ $+42\cdot5°$.

dl-*Threo*-$\alpha\gamma\delta$-*trihydroxyvaleric acid phenylhydrazide*, prepared by the union of the antipodes, crystallises in needles, m. p. 128—130°, and is a true racemate.

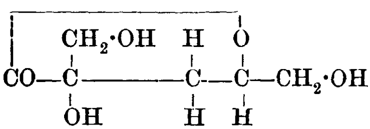
IV. *d*-Galactose with 8*N*-sodium hydroxide yields much less *dl*-lactic acid than dextrose, but, on the other hand, far more *dl*-$\alpha\gamma$-dihydroxybutyric acid.

The compound previously described (Abstr., 1908, i, 8) as giving brucine *dl-para*saccharinate, m. p. 193—194°, is in reality *dl*-α-hydroxybutyrolactone.

*meta*Saccharin and *para*saccharin are stereoisomerides, and correspond with the α- and β-*d*-galacto*meta*saccharinic acids. Accordingly, the four *para*saccharinic acids disappear from the literature.

[With LUCAS]—The *lactone* of *α-hydroxymethyl-*d*-lyxonic acid*, prepared by the oxidation of an alkaline solution of galactose with air, forms crystals, m. p. 107—108°, $[\alpha]_D^{20}$ + 82·3°. The *brucine* salt crystallises in transparent, flat needles, m. p. 166°, $[\alpha]_D^{20}$ − 27·6°; the *quinine* salt has m. p. 162°, $[\alpha]_D^{20}$ − 107·5°; the *phenylhydrazide* has m. p. 162°, $[\alpha]_D^{20}$ − 11·06°. The lævulosecarboxylic acid, prepared by the addition of hydrogen cyanide to lævulose, has the formula of an α-hydroxymethyl-*d*-gluconic acid; apparently the addition of hydrogen cyanide is entirely asymmetric, as no isomeric lævulosecarboxylic acid is formed.

α-*d*-*iso*Saccharin (annexed formula) crystallises in heavy, measurable crystals, m. p. 96°, $[\alpha]_D^{20}$ + 61·9°. Characteristic are the calcium and quinine salts described by Kiliani (Abstr., 1904, i, 373). The *brucine* salt forms pointed needles, m. p. 164°; the *phenylhydrazide* forms needles, m. p. 120—122°, $[\alpha]_D^{20}$ + 19·6°.



α-*d*-Galacto*meta*saccharin (compare Kiliani, Abstr., 1905, i, 737) has m. p. 144°, $[\alpha]_D^{20}$ − 45·3°. The *brucine* salt forms transparent, hexagonal plates, m. p. 140°, $[\alpha]_D^{20}$ − 12·74°; the *strychnine* salt has decomp. 185—195°, $[\alpha]_D^{20}$ − 8·41°; the *barium* salt has $[\alpha]_D^{20}$ + 27·4°.

β-*d*-Galacto*meta*saccharin (Kiliani's *para*saccharin). The *strychnine* salt has m. p. 125—130°, $[\alpha]_D^{20}$ − 23°.

These α- and β-acids are related in the same manner as gluconic and mannonic acids, and are converted into one another on heating above 200°.

α-*d*-Galacto*meta*saccharonic acid (Kiliani, Abstr., 1885, 745) has m. p. 155°, $[\alpha]_D^{20}$ + 22·25°. The disodium salt has $[\alpha]_D$ + 19·11°. The β-isomeride (Kiliani, Abstr., 1904, i, 373, 975) forms a lactone, m. p. 159—160°, $[\alpha]_D^{20}$ − 98·05°; the disodium salt has $[\alpha]_D$ − 18·23°.

These isomeric *d*-$\alpha\gamma\delta$-trihydroxyadipic acids are readily converted when heated with acetic anhydride into *γ-hydroxymuconolactone*, $\begin{matrix}CH{:}CH\\ |\\ CO—O\end{matrix}\!>C{:}CH{\cdot}CO_2H$, which crystallises in transparent, yellow plates, m. p. 228—230°.

V. Dextrose with 8*N*-sodium hydroxide yields a considerable quantity of *dl*-lactic acid, and about 25% of saccharins, mainly α- and β-*d*-dextro*meta*saccharin, with relatively little *iso*saccharin. There is also but little resin produced.

β-Dextro*meta*saccharin, m. p. 92°, $[\alpha]_D^{20}$ + 8·2°, forms a sparingly soluble *calcium* salt, $[\alpha]_D^{20}$ − 23·25°, a *brucine* salt crystallising in long, transparent, rectangular plates or needles, decomp. 130—150°,

$[\alpha]_D^{20}$ $-33\cdot14°$, a *strychnine* salt, decomp. 180—190°, $[\alpha]_D^{20}$ $-30\cdot79°$, a *quinine* salt, m. p. 150—155°, $[\alpha]_D^{20}$ $-113\cdot6°$, and a *phenylhydrazide*, m. p. 124—126°, $[\alpha]_D^{20}$ $-30\cdot7°$.

α-*Dextro*meta*saccharin*, m. p. 104°, $[\alpha]_D^{20}$ $+25\cdot28°$, gives a soluble *calcium* salt, a *brucine* salt crystallising in transparent plates, m. p 150°, $[\alpha]_D^{20}$ $-23\cdot14°$, a *strychnine* salt, m. p. 146°, $[\alpha]_D^{20}$ $-19\cdot5°$, a *quinine* salt, colourless needles, m. p. 135—140°, $[\alpha]_D^{20}$ $-100\cdot9°$; *phenylhydrazide* has m. p. 100—103°, and is optically inactive.

α-d-*Dextro*meta*saccharonic acid* has $[\alpha]_D^{20}$ $-1\cdot36°$, yields a sparingly soluble characteristic *calcium* salt, and forms a *sodium* salt, $[\alpha]_D^{20}$ $-3\cdot97°$. The β-isomeride exists only as a *lactone* crystallising in prisms, m. p. 165°, $[\alpha]_D^{20}$ $-4\cdot73$; the *sodium* salt has $[\alpha]_D^{20}$ $-35\cdot22°$. Both these give γ-hydroxymuconic lactone when heated with acetic anhydride. Considerations based partly on the optical activity enable space formula to be assigned to all these acids.

VI. Formose synthesised from formaldehyde by means of lead hydroxide yields with 8*N*-sodium hydroxide a mixture of saccharins, in which C_5 and C_6 derivatives are present in equal quantities, indicating that formose consists about one half of hexoses and one half of pentoses.

VII. Any carbohydrate in weak alkaline solution is eventually converted into an equilibrium mixture in which one hundred and sixteen substances can take part, namely, the thirty-two aldoses with one to six carbons, the thirty-two corresponding methylenenols, the twenty-six ketoses with three to six carbons in an unbranched chain, and the twenty-six olefineols, that is, dienols. Methylenenols are continually polymerised to dienols; diose molecules give 2:3-dienols of tetroses. Methylenenols of aldotetroses cannot polymerise with one another or with C_3 molecules to octoses or heptoses, but they unite with hydroxymethylene or diosemethylenenol to αβ pentose- and βγ-hexose-dienols, from which the pentoses and hexoses are formed. The synthesis of sugar from formaldehyde never goes further than hexose. There is also no condensation of 6-hydroxymethylene molecules to inositol.

The fact that mannose, dextrose, and lævulose remain unchanged in aqueous solution proves that no trace of αβ-dienol,

$$OH\cdot CH:C(OH)\cdot[CH(OH)]_3\cdot CH_2\cdot OH,$$

is present. This enol and the isomeric aldoses are considered to be three entirely different substances having no tautomeric relation to one another.

In the formation of lævulic and formic acids on heating 2-ketohexoses with acids, 4-hydroxymethylfurfuraldehyde,

$$CHO\cdot \underbrace{C:CH\cdot CH:C}_{O}\cdot CH_2\cdot OH,$$

is formed as an intermediate product, and the colour reactions with phenols are due to the formation of condensation products with this aldehyde. Mannose, dextrose, and galactose yield this aldehyde on heating with oxalic acid (Blanksma and Alberda van Ekenstein, Abstr., 1909, i, 228; this vol., i, 130, 461), due to a αβ-enolisation and conversion into β-ketohexose. Similarly, Fenton (Trans., 1901, **79**, 36, 807; 1909, **95**, 1334) has shown that 4-halogenmethylfurfuraldehyde is obtained from lævulose and more slowly from the aldohexoses on treatment with dry halogen hydride. Carbohydrates behave therefore very differently towards acids and alkalis. E. F. A.

Hexose Phosphoric Acid Ester. A. VON LEBEDEFF (*Biochem. Zeitsch.*, 1910, **28**, 213—229. Compare Abstr., 1909, i, 863).—The same hexose phosphoric acid ester is formed from dextrose and lævulose on fermentation with yeast juice. The compound with phenylhydrazine is considered to be the *phenylhydrazino-phosphoric acid* compound of a hexosazone, $C_{24}H_{31}O_7N_6P$, that is, $C_6H_8N_2,H_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$. It crystallises in canary-yellow bunches of needles of silky lustre, m. p. 148—150° (decomp.). When heated with hydrochloric acid, the corresponding *hexosonephosphoric acid* ester is formed; it yields an amorphous, sparingly soluble *lead* salt. When heated with potassium hydroxide, the hydrazinohexosazone yields dextrosazone and glyoxalosazone.

The hexose phosphoric ester forms a colourless, amorphous *phenylhydrazone*, also a p-*bromophenylhydrazone* crystallising in colourless needles, m. p. 128° (decomp.). The p-*bromophenylosazone* is yellow, m. p. 165°.

The ester is a compound of 1 mol. of carbohydrate and 1 mol. of phosphoric acid, which latter cannot be attached to the two terminal groups which react with phenylhydrazine. It is apparently different from the compound described by Young (Proc., 1907, **23**, 65), and also differs from the glucophosphoric acid prepared by Neuberg and Pollak (this vol., i, 157, 610), which reacts with phenylhydrazine, forming glucosazone, and does not form a sparingly soluble phenylhydrazone.

E. F. A.

A Simple Method for the Preparation of Glucosamine Hydrochloride from Ovomucoid. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1910, **68**, 173—180).—By warming ovomucoid for about an hour with 3% hydrochloric acid, glucosamine hydrochloride is obtained from the products by simply concentrating on the water-bath. It then crystallises out. Ovomucoid contains glucosamine as such, not as a polymeric product. W. D. H.

Derivatives of Lactose and of Maltose and Two New Glucosides. EMIL FISCHER and HANS FISCHER (*Ber.*, 1910, **43**, 2521—2536).—The method of synthesing disaccharides by the interaction of "β-bromoacetodextrose" and silver carbonate (Fischer and Delbrück, Abstr., 1909, i, 633) has been applied to "bromoacetolactose" and "bromoacetomaltose" with the expectation of obtaining tetrasaccharides. The hope has been partially fulfilled in the former case. A solution of "bromoacetolactose" in dry chloroform is shaken with freshly precipitated, dried silver carbonate, whereby a *substance*, $C_{24}H_{28}O_7(OAc)_{14}$, is obtained, which is probably the tetradeca-acetyl derivative of a tetrasaccharide; after purification by alcohol, it consists of a colourless, granular, indistinctly crystalline powder, which melts in boiling water. A sample, purified by shaking with dilute potassium hydroxide, has $[\alpha]_D^{21}$ +20·69° in chloroform. By hydrolysis in acetone with cold aqueous barium hydroxide, a substance is obtained, which, on account of its slight reducing action on Fehling's solution and the formation of a little phenyl-lactosazone with phenylhydrazine, is regarded as a mixture of about 25% of lactose (or of a substance which is easily converted into lactose) and a non-reducing carbo-

hydrate of high molecular weight, probably a tetrasaccharide; unfortunately, all attempts to obtain the latter in a pure state have been unsuccessful.

The interaction of "chloroacetomaltose" (or of the impure "bromoacetomaltose" described below) and freshly precipitated silver carbonate in moist ether yields *hepta-acetylmaltose*, $C_{26}H_{36}O_{18}$ m. p. 179—180° (corr.), which separates from alcohol in slender needles, strongly reduces warm Fehling's solution, and exhibits slight mutarotation, having $[\alpha]_D^{16}$ +72·62° to 76·66° in acetylene tetrachloride. From its method of formation it should be constituted similarly to hepta-acetylcellobiose (following abstract) and tetra-acetyldextrose, but it differs from these by its sparing solubility in dilute alkali.

The difficulty of obtaining crystallised "bromoacetomaltose" led the authors to examine the action of acetyl bromide on maltose. The direct interaction of the two substances, moderated by occasional cooling of the containing flask in a freezing mixture, yields a somewhat impure, amorphous bromohepta-acetylmaltose, which, however, can be used for the preceding and for the following experiment. *Hepta-acetylmenthylmaltoside*, $C_{36}H_{54}O_{18}$, m. p. 186° (corr.), obtained by shaking "bromoacetomaltose," dry silver carbonate, menthol, and ether for several hours, crystallises in needles, is odourless, does not reduce Fehling's solution, and has $[\alpha]_D^{19}$ +20·84° in *s*-tetrachloroethane. When its hot alcoholic solution is hydrolysed by boiling aqueous barium hydroxide, *menthylmaltoside*, $C_{22}H_{40}O_{11}$, m. p. 203° (corr.), $[\alpha]_D^{16}$ +14·23° in aqueous solution, is obtained, which separates from water in needles containing $2H_2O$, has an unpleasant taste, does not reduce Fehling's solution, and forms a *barium* salt, $(C_{22}H_{39}O_{11})_2Ba$.

The preparation of "bromoacetolactose" (bromohepta-acetyl-lactose) by Ditmar's method with acetyl bromide and dry lactose frequently miscarries from unknown causes. Therefore the authors employ the following very convenient method. A solution of octa-acetyl-lactose in acetic anhydride is treated with a saturated solution of hydrogen bromide in glacial acetic acid; after one hour and three-quarters at 15—20°, the mixture is poured into water at 0°, the precipitate is dissolved in chloroform, and is recovered by the addition of light petroleum to the washed and dried solution. By rapid crystallisation from warm alcohol the substance is obtained quite pure, and has m. p. 143—144° (corr.), and $[\alpha]_D^{22}$ +104·9° in chloroform. This method has also been employed in the preparation of "*β-iodoacetodextrose*," $C_{14}H_{19}O_9I$, m. p. 110—111° (corr.), $[\alpha]_D^{20}$ +231·9° in *s*-tetrachloroethane, from *α*- or *β*-penta-acetyldextrose in acetic anhydride, and hydrogen iodide in glacial acetic acid; it crystallises in colourless needles, and belongs probably to the *β*-series, since it is converted into tetra-acetyl-*β*-methyl glucoside by methyl alcohol and silver carbonate, in which case, therefore, its formation from *α*-penta-acetyldextrose must be accompanied by intramolecular change.

Hitherto synthetic glucosides of polyhydric alcohols have not been obtained in the crystalline state. This has now been achieved by the use of pure "bromoacetodextrose," which has the great advantage of forming easily crystallisable acetyl derivatives. *Tetra-acetyl-β-glycolglucoside*, $C_{16}H_{24}O_{11}$, m. p. 101—103° (corr.), obtained by shaking

glycol, pure bromoacetodextrose, and dry silver carbonate for several hours, crystallises from water in stout prisms, does not reduce Fehling's solutions, has $[\alpha]_D^{16}$ $-26{\cdot}23°$ in aqueous solution, and is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding *β-glycol-d-glucoside*, $C_8H_{16}O_7$, m. p. 137—138 (corr.), $[\alpha]_D^{16}$ $-30{\cdot}20°$ in aqueous solution, which can be obtained in stout crystals by the slow evaporation of its solution in alcohol–ethyl acetate, rapidly by inoculation when crystals have once been secured; it does not reduce Fehling's solution, and is rapidly hydrolysed by hot mineral acids and by emulsin, which indicates that the glucoside belongs to the β-series.

B. HELFERICH, by the preceding method, has obtained crystalline *d*-glucosides of benzyl alcohol, $[\alpha]_D^{20}$ $-55{\cdot}6°$, of *cyclo*hexanol, $[\alpha]_D^{20}$ $-41{\cdot}5°$, of geraniol, $[\alpha]_D^{27}$ $-37{\cdot}3°$, of cetyl alcohol, $[\alpha]_D^{18}$ $-22{\cdot}5°$, and of glycollic acid, $[\alpha]_D^{20}$ $-43{\cdot}8°$. C. S.

Derivatives of Cellobiose. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1910, **43**, 2536—2543. Compare preceding abstract).—The experiments on cellobiose and their results are quite similar to those in the case of lactose. "*Bromoacetocellobiose*," $C_{12}H_{14}O_{10}BrAc_7$, is obtained by shaking octa-acetylcellobiose at the ordinary temperature with a solution of hydrogen bromide in glacial acetic acid saturated at 0°; it crystallises in needles, darkens at 180°, and melts and decomposes a few degrees higher, and has $[\alpha]_D^{20}$ $+96{\cdot}54°$ in chloroform. "*Iodoacetocellobiose*," $C_{12}H_{14}O_{10}IAc_7$, prepared in a similar manner (the isomeric octa-acetylcellobiose, m. p. 198°, may be used), forms needles, has m. p. 160—170° (decomp.), and $[\alpha]_D^{20}$ $+125{\cdot}6°$ in chloroform and 123·2° in *s*-tetrachloroethane. From either of these compounds, by boiling with water and calcium carbonate, or by shaking with silver carbonate in a moist solvent, most conveniently in acetone, *hepta-acetylcellobiose*, $C_{12}H_{15}O_{11}Ac_7$, m. p. 195—197°, is obtained, which crystallises from water in slender needles, has $[\alpha]_D^{20}$ $+19{\cdot}95°$ in chloroform, 19·58° in *s*-tetrachloroethane, and 18·85° after twenty minutes and 25·48° after twenty-six hours in methyl alcohol; it dissolves easily in cold, very dilute sodium hydroxide, and is not re-precipitated by acids. When "bromoacetocelloboise" is shaken with dry silver carbonate in dry chloroform for a few hours, a colourless, granular powder is ultimately obtained, which is a mixture consisting chiefly of the *tetradeca-acetyl* derivative of a tetrasaccharide, $C_{24}H_{28}O_{21}Ac_{14}$; by hydrolysis in acetone with cold saturated barium hydroxide it is converted into a substance, $[\alpha]_D^{20}$ 18·7° in water, which consists of a carbohydrate of high molecular weight mixed with about 30% of cellobiose, the amount of which is deduced from the reducing power of the substance and the weight of phenylcellobiosazone produced with phenylhydrazine. The carbohydrate has not been isolated in a pure state. C. S.

Destructive Distillation of Cellulose. ERNST ERDMANN and C. SCHAEFER (*Ber.*, 1910, **43**, 2398—2406).—The following substances have been obtained by subjecting cellulose to destructive distillation from a copper retort during two hours: (*a*) Gas containing carbon dioxide 0·2, heavy hydrocarbons 0·5, oxygen 0·9, carbon monoxide 65·5, methane 19, hydrogen 11·5, nitrogen 2·4 per cent.; (*b*) aqueous

liquid, about 40% of the original cellulose; this forms a reddish-brown liquid with a pungent odour, is strongly acidic, has reducing properties, and gives a deep purple coloration with ferric chloride; (c) brown mobile tar, 5% of the cellulose.

The following products have been isolated from the aqueous distillate after neutralising with sodium carbonate and subjecting to fractional distillation: Formaldehyde; furfuraldehyde; maltol (compare Brand, Abstr., 1894, i, 270; Kiliani and Balzen, Abstr., 1895, i, 80; Peratoner and Tamburello, Abstr., 1905, i, 807); ω-hydroxymethylfurfuraldehyde, the semioxazone of which is not molten at 260°, and γ-valerolactone. J. J. S.

Insoluble Lead Salts of Amino-acids. PHŒBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1910, 8, 285—286).—Both tyrosine and aspartic acid form lead salts which are nearly insoluble in water. The fact will probably be useful in the separation of these amino-acids from mixtures. W. D. H.

Synthesis of Polypeptides. Derivatives of *l*-Leucine. EMIL ABDERHALDEN and L. E. WEBER (*Ber.*, 1910, 43, 2429—2435).—The complicated polypeptides afford materials for the study of the peptolytic enzymes. *d*-Alanyl-glycyl-glycine ($[\alpha]_D + 31°$) is hydrolysed by some enzymes to *d*-alanine and inactive glycyl-glycine as shown by a decrease in rotatory power. The pressed juice of cancer cells causes an increase in rotatory power, indicating hydrolysis to glycine and *d*-alanylglycine.

In order to have further test materials available, a number of new polypeptides have been prepared containing *l*-leucine and glycine. It is found that the introduction of each glycine group causes a large increase in lævorotation, an introduction of leucine working in the contrary direction.

Chloroacetyl-l-*leucine*, prepared by coupling the constituents in presence of sodium hydroxide, has m. p. 139—140° (corr.), $[\alpha]_D^{20} - 13{\cdot}1°$. By the action of ammonia at 37°, *glycyl*-l-*leucine* is formed, crystallising in plates which turn brown at 246° (corr.), m. p. 256° (corr., decomp.), $[\alpha]_D^{20} - 31°$. From the mother liquors an insoluble compound crystallising in plates, m. p. 223° (corr.), was obtained.

d-α-*Bromo*iso*hexoyl-glycyl*-l-*leucine* crystallises in needles, m. p. 101° (corr.), $[\alpha]_D^{20} + 30{\cdot}4°$.

l-*Leucylglycyl-leucine*,

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(C_4H_9){\cdot}CO_2H,$$

is obtained as a granular powder, m. p. 256—266° (decomp.), $[\alpha]_D^{20} + 6{\cdot}0°$.

Chloroacetyl-l-*leucyl-glycyl*-l-*leucine* is obtained in small, hygroscopic needles, which soften at 70°, $[\alpha]_D^{20} - 9{\cdot}1°$.

Glycyl-l-*leucyl-glycyl*-l-*leucine* is a granular powder which becomes brown at 240°, m. p. 256—257° (corr.), $[\alpha]_D^{20} - 51{\cdot}0°$.

l-*Leucyl-glycyl*-l-*leucyl-glycyl*-l-*leucine* is a crystalline powder which becomes brown at 210°, m. p. 256—266° (corr., decomp.), $[\alpha]_D^{20} - 14{\cdot}5°$.

E. F. A.

Synthesis of Polypeptides. Derivatives of *iso*Leucine. III. EMIL ABDERHALDEN and PAUL HIRSCH (*Ber.*, 1910, **43**, 2435—2441. Compare Abstr., 1909, i, 769).—*l*-Leucyl-*d*-*iso*leucine has $[\alpha]_D^{20}$ $+18{\cdot}13°$, and shows no biuret reaction.

l-*Leucyl*-d-iso*leucine anhydride*,

$$CHMe_2{\cdot}CH_2{\cdot}CH{<}^{NH{\cdot}CO}_{CO{\cdot}NH}{>}CH{\cdot}CHMeEt,$$

forms slender needles, m. p. 291° (corr.), $[\alpha]_D^{20}$ $-35{\cdot}76°$.

d-*α-Bromopropionyl*-l-*leucyl*-d-iso*leucine*, prepared by coupling the constituents in the usual manner, sinters at 153°, m. p. 164° (corr.), $[\alpha]_D^{20}$ $-23{\cdot}37°$.

d-*Alanyl*-l-*leucyl*-d iso*leucine* forms minute needles, sinters at 231°, and has m. p. 245° (corr., decomp.). In *N*-hydrochloric acid it has $[\alpha]_D^{20}$ $-24{\cdot}89$; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ $-45{\cdot}72°$; in water, $[\alpha]_D^{20}$ $-9{\cdot}12°$. The tripeptide gives a violet biuret reaction and forms a *copper* salt.

Chloroacetyl-d-*alanyl*-l-*leucyl*-d-iso*leucine* separates in tiny needles, which sinter at 189°, m. p. 197°, $[\alpha]_D^{20}$ $-54{\cdot}83°$.

Glycyl-d-*alanyl*-l-*leucyl*-d-iso*leucine*, obtained by the action of ammonia on the previous compound, sinters at 231°, m. p. 251° (corr., decomp.). In *N*-hydrochloric acid, it has $[\alpha]_D^{20}$ $-80{\cdot}59°$; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ $-78{\cdot}44°$. It shows a pronounced biuret coloration, and forms a *copper* salt. E. F. A.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVI. Action of Ammonia and Amines on Thiocarbonates. MARCEL DELÉPINE and PAUL SCHVING (*Bull. Soc. chim.*, 1910, [iv], **7**, 894—902).—The action of ammonia and of primary and secondary amines on thiocarbonates of the following five types has been studied: $SR_1{\cdot}CS{\cdot}SR_2$, $OR_1{\cdot}CS{\cdot}SR_2$, $OR_1{\cdot}CS{\cdot}OR_2$, $SR_1{\cdot}CO{\cdot}SR_2$, $OR_1{\cdot}CO{\cdot}SR_2$.

With ammonia at atmospheric temperatures there are formed in the course of three or four days, urethanes of the following types respectively for the compounds indicated above: $SR_1{\cdot}CS{\cdot}NH_2$, $OR_1{\cdot}CS{\cdot}NH_2$, $OR_1{\cdot}CS{\cdot}NH_2$, $SR_1{\cdot}CO{\cdot}NH_2$, $OR_1{\cdot}CO{\cdot}NH_2$. In the cases of types two and three some ammonium thiosulphate is formed, not as Salomon supposed (this Journ., 1873, 617), due to the presence of impurities, but to atmospheric oxidation (compare Husemann, *Annalen*, 1862, **123**, 68; **126**, 297, and Conrad and Salomon, this Journ., 1875, 753). With ammonia at 100° the three first types yield ammonium thiocyanate, and types four and five, carbamide.

Primary amines react in a manner strictly analogous to ammonia, furnishing at atmospheric temperature, and in the course of several days, the corresponding urethanes, thus: $SR_1{\cdot}CS{\cdot}NHR_3$, $OR_1{\cdot}CS{\cdot}NHR_3$ $OR_1{\cdot}CS{\cdot}NHR_3$, $SR_1{\cdot}CO{\cdot}NHR_3$, $OR_1{\cdot}CO{\cdot}NHR_3$. With excess of the primary amine at 100° the corresponding dialkylcarbamides are formed, the action taking place very slowly in the case of type two, where the ester used was $SMe{\cdot}CS{\cdot}OMe$, and the amine, ethylamine, but similar results were obtained with aniline.

With secondary amines the action tends to remain at the urethane stage even with excess of the am ne at 100—120°.

Dimethyl trithiocarbonate, $CS(SMe)_2$, D_4^0 1·2820, D_4^{21} 1·2630, b. p 225°, is an orange-yellow, highly refractive oil of peculiar odour (compare Cahours, *Ann. Chim. Phys.*, 1847, [iii], **19**, 158).

Ethyl diethylthioncarbamate, NEt_2·CS·OEt, b. p. 224°, is a colourless liquid. *Methyl piperidylthioncarbamate*, $C_5H_{10}N$·CS·OMe, m. p. 23°, b. p. 120—122°/16 mm., obtained by the action of piperidine on methyl thiothioncarbonate, OMe·CS·SMe, is crystalline, possesses a mint-like odour, evolves sulphuric acid vapours at 100°, and phosphoresces (compare this vol., i, 295). *Propyl thioncarbamate*,

OPr^α·CS·NH_2,

m. p. 35°, formed by the action of ammonia on the ester,

OPr^α·CS·SMe,

is crystalline. *Methyl dimethylthiocarbamate*, NMe_2·CO·SMe, D_4^0 1·1098, D_4^{22} 1·0895, b. p. 180°, obtained by the action of dimethylamine on methyl dithiocarbonate, $CO(SMe)_2$, is a colourless liquid with a fungoid odour. T. A. H.

Colour of Vanadium Thiocyanate. C. BONGIOVANNI (*Boll. chim. farm.*, 1910, **49**, 467—468).—When a solution of vanadium sulphate is treated with barium thiocyanate, a green liquid is obtained, and it has consequently been supposed that vanadium thiocyanate is green, in contradistinction to the vanadithiocyanates of the alkali metals, which are violet. The author advances reasons for the view that the green colour is a result of hydrolytic processes due to the presence of sulphates. Vanadium chloride and thiocyanic acid give an intense reddish-violet coloration, which becomes green on addition of sulphates, or of ammonium oxalate or acetate. These substances also decolorise the red solution obtained when a ferric salt is treated with a thiocyanate. It appears probable, therefore, that vanadium thiocyanate has a colour similar to that of the vanadithiocyanates.

R. V. S.

New Method for the Preparation of Aliphatic Nitriles. ALEXANDER E. ARBUSOFF (*Ber.*, 1910, **43**, 2296—2300).—Good yields of aliphatic nitriles can be obtained by heating the phenylhydrazones of some of the higher aliphatic aldehydes with metallic salts, such as cuprous chloride, platinous chloride, or zinc chloride. The reaction proceeds according to the equation:

$$C_5H_{10}:N\cdot NHPh = NH_2Ph + C_5H_9N.$$

The following nitriles have been prepared by heating the phenylhydrazone with a small amount of cuprous chloride (0·2 gram) at 180—200°, and subjecting the products to fractional distillation under reduced pressure: *iso*valeronitrile, 56%; *iso*butyronitrile, 37%; heptonitrile, 60% yield. J. J. S.

The Supposed Lead Ferricyanide is a Lead Ferricyanide-nitrate. ERICH MÜLLER and OTTO DIEFENTHÄLER (*Ber.*, 1910, **43**, 2321—2323).—The dark red precipitate which is obtained by the interaction of solutions of lead nitrate and potassium ferricyanide is

not lead ferricyanide, as has hitherto been supposed, but lead ferricyanide-nitrate, $Pb_2[Fe(CN)_6]NO_3,5H_2O$.

It is suggested that the constitution is either $NO_3{\cdot}Pb{\cdot}Pb{\vdots}FeC_6N_6$ or $Pb{\vdots}Fe(C_6N_6){\cdot}Pb{\cdot}NO_3$, and the fact that the dark red crystals give a light greenish-yellow solution indicates that there may be an equilibrium between these two forms. T. S. P.

The Action of Hydrogen Aurichloride on Aqueous Solutions of Potassium Ferrocyanide. ERNST BEUTEL (*Monatsh.*, 1910, **31**, 871—881).—The reaction between hydrogen aurichloride and potassium ferrocyanide in aqueous solution depends on the relative proportions of the two reagents. In the first experiments a solution containing 4·6400 grams of hydrogen aurichloride and 8·5356 grams of potassium ferrocyanide per litre was used, this corresponding with 4 mols. of the former to 3 mols. of the latter compound. The solution, when made, rapidly became emerald-green, changing to deep blue in the course of twelve hours. At the end of eight days, during which the solution was exposed to sunlight in a sealed flask, a deep blue precipitate had deposited, leaving a colourless, supernatant liquid. The precipitate consisted of pure ferric ferrocyanide, and the supernatant liquid contained the aurocyanide, auricyanide, and aurichlorocyanide of potassium, potassium chloride, and hydrochloric acid. The quantitative results were in accordance with the equation: $28HAuCl_4 + 21K_4FeC_6N_6 = 8KAuC_4N_4 + 6KAuC_2N_2 + 14KAuCl_2C_2N_2 + 56KCl + 28HCl + 3Fe_4(FeC_6N_6)_3$. The reaction products could not, for the most part, be isolated from the solution, owing to the fact that on concentration the complex cyanides are decomposed by the hydrochloric acid with the formation of aurous cyanide. Potassium auricyanide was isolated, since it resists the action of the mineral acid to a great extent.

The supernatant liquid already mentioned will enter into further reaction with the two reagents. With hydrogen aurichloride, it turns sulphur-yellow, and aurous cyanide is precipitated after a short time. With potassium ferrocyanide, it turns green, and then gives a bluish-green precipitate of a mixture of ferric hydroxide and ferric ferrocyanide. On long exposure to the light, the precipitate becomes pure ferric hydroxide only. Exact equations could not be given for these reactions.

In the next series of experiments, approximately equimolecular solutions of the two reagents (10 grams of hydrogen aurichloride per litre $= A$; 10 grams of potassium ferrocyanide per litre $= B$) were mixed in varying proportions. With mixtures varying from $3A : B$ to $25A : B$, the chief reaction is the precipitation of aurous cyanide. With $A : B$, the solution gradually changes from a light green to a dark brown, and retains the latter colour for a long time in diffused daylight or in the dark, no precipitate being formed. On exposure to sunlight, the colour changes to emerald-green, then dark blue, and finally disappears, a dark blue precipitate being deposited. With $A : 2B$ an emerald-green solution is obtained immediately, and the solution gradually, quicker on warming, deposits blue ferric ferrocyanide, leaving a yellow supernatant liquid containing the excess of potassium ferrocyanide. Similar results are obtained with $A : 3B$ and

$A:5B$, but the blue precipitate takes much longer to form. With $A:10B$ and $A:25B$, green solutions are obtained, which only on long keeping in sunlight deposit small quantities of ferric hydroxide, leaving a yellow solution containing ferro- and ferri-cyanide.

Potassium ferricyanide behaves similarly to potassium ferrocyanide towards hydrogen aurichloride, but a quantitative investigation is still wanting. T. S. P.

Action of Aqueous Solutions of Potassium Ferrocyanide on Aurous Cyanide and Gold Hydroxide. ERNST BEUTEL (*Monatsh.*, 1910, **31**, 883—886).—When aurous cyanide is heated with a solution of potassium ferrocyanide, oxygen being passed through the solution during the heating, it dissolves with the formation of potassium aurocyanide, ferric hydroxide being precipitated according to the equation:

$$8AuCN + 2K_4FeC_6N_6 + 5H_2O + O = 8KAuC_2N_2 + 2Fe(OH)_3 + 4HCN.$$

Gold hydroxide dissolves in a solution of potassium ferrocyanide with the formation of potassium gold cyanide and the precipitation of ferric hydroxide. The reaction takes place at room temperature, but much quicker on warming. Quantitative experiments were not made, and the particular potassium gold cyanide formed is not stated.

Fulminating gold also dissolves in solutions of potassium ferrocyanide. The solution first becomes emerald-green, and hydrogen cyanide is evolved. A green precipitate is then produced, which finally changes to brown ferric hydroxide. Potassium gold cyanide remains in solution. T. S. P.

Solubility of Finely-divided Gold in Solutions of Potassium Ferrocyanide. ERNST BEUTEL (*Monatsh.*, 1910, **31**, 887—890).—Finely-divided gold will dissolve completely in solutions of potassium ferrocyanide at room temperature. The rate of solution is very slow, even at the boiling point. Potassium aurocyanide is formed, and the resulting ferro-ions are oxidised by the oxygen of the air, giving ferric hydroxide. The solution formed is alkaline. The reaction probably takes place according to the equation:

$$3Au + K_4FeC_6N_6 + 2H_2O + O_2 = 3KAuC_2N_2 + Fe(OH)_3 + KOH.$$

T. S. P.

Estimation of Diazo-alkyls. E. K. MARSHALL and SALOMON F. ACREE (*Ber.*, 1910, **43**, 2323—2330).—Wegscheider and Gehringer's statement (Abstr., 1903, i, 685), that the yield of ester obtained by the action of an ethereal solution of diazomethane on an acid is greater than would be expected from the concentration of the diazomethane solution as determined by titration with iodine (Pechmann, Abstr., 1894, i, 438), is confirmed. The same solution of diazomethane does not give concordant results when titrated by the iodine method.

For estimating the concentration of a diazomethane solution, the authors recommend the use of an excess of *m*- or *p*-nitrobenzoic acid in ethereal solution and titrating the excess of acid by means of standard alkali after diluting with water, or actually isolating the methyl ester by extraction with chloroform after shaking with water

and sodium hydrogen carbonate solution. The results are correct to within 2—3%. Low results are obtained in the presence of alcohol.

Diazoethane can be estimated in a similar manner. J. J. S.

The Alkyl and Aryl Compounds of Tin. PAUL PFEIFFER [with R. LEHNHARDT, H. LUFTENSTEINER, RUDOLF PRADE, K. SCHNURMANN, and P. TRUSKIER] (*Zeitsch. anorg. Chem.*, 1910, **68**, 102—122).—A number of organic derivatives of quadrivalent tin have been described, as a preliminary to the study of their molecular compounds for comparison with those of cobalt, chromium, and platinum.

In the preparation of methylstannic acid from methyl iodide and an aqueous-alcoholic solution of potassium stannate, carbon dioxide precipitates small, glistening crystals of *potassium methylstannicarbonate*, $SnMeO \cdot O \cdot CO_2K,H_2O$, an aqueous solution of which decomposes on boiling, yielding methylstannic acid.

Dimethylstannic halides are best prepared by heating tin with methyl iodide, converting the product into oxide by means of ammonia, and then into the chloride by means of hydrogen chloride. After crystallising from light petroleum to remove the monomethyl compound, the chloride is converted into the oxide and then into the required salts. The chloride, bromide, and iodide have m. p.'s 108°, 78°, and 43° respectively. *Dimethylstannic oxalate*, $SnMe_2C_2O_4$, forms a white precipitate, soluble in a solution of potassium oxalate. *Dimethylstannic sulphide* is a white precipitate, soluble in ammonium sulphide.

Dipropylstannic bromide, $SnPr_2Br_2$, forms large, colourless needles, m. p. 49°.

Dibutylstannic oxide, $SnO(C_4H_9)_2$, when prepared by the action of aqueous-alcoholic ammonia on the pure chloride, forms an insoluble, amorphous powder. The *chloride*, $Sn(C_4H_9)_2Cl_2$, is sparingly soluble in water and has m. p. 43°; the *bromide* has m. p. 20°.

Di*iso*amylstannic oxide yields a basic chloride, m. p. 145°, on treatment with hydrochloric acid followed by pyridine.

Tribenzylstannic chloride, $Sn(C_7H_7)_3Cl$ (Abstr., 1904, i, 232), melts at 142—144° after crystallisation from glacial acetic acid. Pyridine is without action on it. Sodium carbonate solution converts it into *tribenzylstannic hydroxide*, $Sn(C_7H_7)_3 \cdot OH$, crystallising in colourless, rhombic tablets, m. p. 117—121°. It is insoluble in water, but soluble in many organic solvents. Acetyl or benzoyl chloride converts it into the chloride, and not into the acetate or benzoate, in this respect resembling the reaction with the corresponding silicon compounds (Robison and Kipping, Trans., 1908, **93**, 439). *Tribenzylstannic bromide* has m. p. 125—128°.

Tin tetrapropyl boils at 228°.

Tin tetra-p-*tolyl*, $Sn(C_6H_4Me)_4$, prepared by the action of magnesium, followed by stannic bromide, on *p*-bromotoluene, forms colourless, glistening needles, m. p. 230°. C. H. D.

Constituents of Coal Tar. VI. *iso*Propylbenzene (Cumene). GUSTAV SCHULTZ (*Ber.*, 1910, **43**, 2517—2521. Compare this vol., i, 897).—[With A. SZÉKELY.]—The viscous, brown, crude acids

obtained by the sulphonation of the "mesitylene" fraction are decomposed by superheated steam, and the resulting hydrocarbons are repeatedly distilled, whereby a fraction, b. p. 150—161°, is obtained, from which cumene is isolated as follows. The fraction is nitrated, and the portion of the product which is easily volatile with steam is fractionally distilled; the chief portion, b. p. 145—150°/30—32 mm., is redistilled, whereby a *nitro*-compound, $C_9H_{11}O_2N$, b. p. 240—245° or 130—133°/15—16 mm., is obtained, which is proved to contain nitrocumene by the following experiments. A portion is reduced by tin and hydrochloric acid, and the amine, b. p. 223—230°, is separated into three fractions, b. p. 223—225°, 225—228°, and 228—230°. The first faction is treated with the calculated quantity of oxalic acid, whereby the oxalates of *p*-cumidine and of *o*-cumidine are obtained; also a portion of the fraction, after being acetylated, yields aceto-*p*-cumidide and acetomesidide. Another portion of the nitro-compound is boiled with 3 parts of nitric acid, D 1·48, and 4·5 parts of water for six days, whereby *p*-nitrobenzoic acid is produced. A third portion yields by further nitration trinitromesitylene and other trinitro-compounds which have not been separated.

A portion, b. p. 150—155°, of the original oil is sulphonated by concentrated and fuming sulphuric acids, and from the products *o*-*iso*-propylbenzenesulphonic acid has been isolated in the form of the sulphonamide, m. p. 96—98°. C. S.

3 : 3′-Dimethyldiphenyleneiodonium Hydroxide and Some of Its Salts. LUIGI MASCARELLI and T. CERASOLI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 308—311. Compare Abstr., 1909, i, 907).—3 : 3′-Dimethyldiphenyleneiodonium iodide is obtained in small quantity by diazotising 6 : 6′-diamino-3 : 3′-dimethyldiphenyl and treating the product with potassium iodide. It yields the above *hydroxide* when treated with moist silver oxide. The *iodide* is a yellow powder, m. p. 246°. The *bromide* is a white powder becoming yellow, m. p. 281°. The *chloride* forms a white, microcrystalline powder, becoming brown, m. p. 290°. The *oxalate*, $\left(\begin{matrix}C_6H_3Me \\ | \\ C_6H_3Me\end{matrix}\!\!>\!I\right)_2C_2O_4$, forms colourless, acicular crystals, m. p. 228°. R. V. S.

Esters of Benzenesulphon-nitroanilides. STANISLAUS OPOLSKI (*Bull. Acad. Sci. Cracow*, 1910, 126—128. Compare Abstr., 1907, i, 908).—To complete the proof that intramolecular change occurs when the three almost colourless benzenesulphon-nitroanilides are converted into their highly coloured salts, it is necessary to isolate the coloured *aci*-esters in addition to the ordinary colourless esters. All attempts to isolate the former, however, have been unsuccessful. By the action of alkyl iodides on the silver salts, the colourless esters are obtained, together with a red oil, from which a crystalline substance cannot be isolated.

The trinitro-compound obtained by the nitration of benzenesulphon-*o*-nitroanilide or of benzenesulphon-*p*-nitroanilide must be benzene-

sulphonpicramide, but attempts to prepare it by the condensation of picramide and benzenesulphonyl chloride, or of picryl chloride and benzenesulphonamide, have been unsuccessful.

*Benzenesulphon-*o*-nitroethylanilide*, $NO_2\cdot C_6H_4\cdot NEt\cdot SO_2Ph$, m. p. 103—104°, and *benzenesulphonbenzyl-*o*-nitroanilide*,

$$NO_2\cdot C_6H_4\cdot N(CH_2Ph)\cdot SO_2Ph,$$

m. p. 148—149°, unlike the colourless methyl esters, have a distinct yellow tinge. *Benzenesulphonmethylpicramide*,

$$(NO_2)_3\cdot C_6H_2\cdot NMe\cdot SO_2Ph,$$

m. p. 181—182°, forms colourless crystals. C. S.

Preparation of Aromatic Alkyl Ethers. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224388).—An extension of the work described in the chief patent (Abstr., 1908, i, 263) to the reaction between substances containing one or more phenolic hydroxyl groups and the nitroso-compounds of acid amides of the general formula $-NR\cdot NO$, where R = alkyl.

The *product* obtained from β-naphthol and nitrosobenzenesulphonethylamide has m. p. 60°. When morphine suspended in methyl alcohol is treated with *p*-toluenesulphononitrosomethylamide in the presence of an alkaline hydroxide, a crystalline *compound*, m. p. 60°, is obtained.

Nitroso-β-naphthalenesulphonomethylamide has m. p. 85°. The morphine and β-naphthol in the foregoing condensations can be replaced by other phenols, cresols, or dihydroxybenzenes. F. M. G. M.

Acenaphthene. FRANZ SACHS and GERHARDT MOSEBACH (*Ber.*, 1910. **43**, 2473—2475).—4-Aminoacenaphthene yields the 4-halogen derivatives of acenaphthene when treated according to the Sandmeyer reaction. An intense dark green coloration is produced on diazotisation. 4-Chloroacenaphthene forms slender needles, m. p. 62·5—63°; 4-bromoacenaphthene has m. p. 51·5° (compare Graebe, Abstr., 1903, i, 408); 4-*iodoacenaphthene* crystallises in rosettes of colourless, slender needles, m. p. 63—63·5° [compare Crompton, Proc. 1910, **26**, 226]. E. F. A.

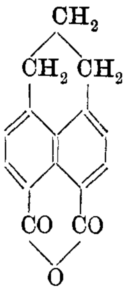
Structure of Pyrene. EGON LANGSTEIN (*Monatsh.*, 1910, **31**, 861—870. Compare Goldschmiedt, Abstr., 1907, i, 310).—The formulæ for pyrene and pyrenic acid deduced by Goldschmiedt are confirmed by isolation of two isomeric methyl hydrogen pyrenates,

$$C_{16}H_{10}O_5.$$

The *a-ester*, prepared by heating the anhydride with a large excess of pure methyl alcohol, crystallises in large needles of a golden-yellow colour and yields golden-yellow solutions. The *β-ester* crystallises in yellowish-green, slender needles, usually arranged in nodules; its solutions are brownish-green, and it is twice as soluble in alcohol as the α-ester. When heated, the β-ester turns brown more rapidly than the α-ester, and decomposes more quickly.

peri-*Trimethylenenaphthalic anhydride* (formula I) is obtained when pyrenic acid is reduced by boiling with hydriodic acid (D 1·96)

and red phosphorus. It crystallises from alcohol in colourless, glistening needles, decomposing at about 260° Its solution in concentrated sulphuric acid has a deep blue fluorescence, and its alcoholic solution a green fluorescence. The corresponding *acid*, $C_{15}H_{12}O_4$, is colourless, and does not readily yield crystalline salts. When the barium salt is heated with lime, peri-*trimethylenenaphthalene*, $C_{13}H_{12}$, is obtained, and this crystallises from dilute alcohol in colourless, glistening plates, m. 68—69°. It turns yellow on exposure to the air, and yields a *picrate* in the form of glistening, red needles, m. p. 127° after turning brown at 80°. The formation of this picrate is used as an argument in favour of the constitutional formula ascribed to the hydrocarbon, as hydronaphthalenes do not yield picrates.



(I.)

Hexahydropyrene (Goldschmiedt, *loc. cit.*) has m. p. 129—130°, and in the presence of excess of picric acid yields a red *picrate*, m. p. 119°. The constitution ascribed to the hexahydro-compound is therefore that of a di*peri*ditrimethylenenaphthalene. J. J. S.

Reduction of Nitrobenzene to Aniline. C. Nicolescu Otin (*Zeitsch. Elektrochem.*, 1910, **16**, 674—680).—The author has tried most of the methods which have been proposed for reducing nitrobenzene to aniline by electrolysis. His results are tabulated, and show that the yields of aniline are usually poor (from 19 to 88%); considerable quantities of other materials are consumed in many of the processes, and undesirable by-products are often formed. He shows that the conditions necessary for a good yield are a very large cathode surface and a considerable excess of hydrochloric acid.

Using 120 c.c. of hydrochloric acid (D 1·19) to 20 grams of nitrobenzene and a cathode consisting of lead wool, or nickel wire in sufficient quantity to fill the whole cathode compartment (the anode is a lead cylinder immersed in sulphuric acid contained in a porous pot), he obtains 92 to 94% of the theoretical quantity of aniline with a current efficiency of 94 to 97%. T. E.

[Chromoisomeric and Homochromoisomeric Nitroanilines.] Arthur Hantzsch (*Ber.*, 1910, **43**, 2516. Compare this vol., i, 475). —The following corrections are made. Priority is given to Flürscheim in the preparation of *s*-nitrophenylenediamine. *o*-Tolyl-2 : 4-dinitroaniline darkens at 120°, and has m. p. 128—129°. Also, a reply is given to Busch (this vol., i, 617) on the isomerism of the two picrylmethylanilines. C. S.

[Preparation of Derivatives of *p*-Toluenesulphon-*p*-nitroanilide.] Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 224499).—*p*-Toluenesulphon-*p*-nitroanilide when treated with methyl chloride yielded p-*toluenesulphonmethyl*-p-*nitroanilide*, m. p. 175—176°; this on reduction with sodium sulphide was converted into p-*toluenesulphonylmethyl*-p-*phenylenediamine*, m. p. 135°, a grey powder some-

what readily soluble in alcohol, more sparingly so in benzene. This base was diazotised and combined in alkaline solution with 8-acetylamino-1-naphthol-3 : 6-disulphonic acid (or similar acids), and the separated product treated during several hours with sulphuric acid at a temperature of 15—20°, whereby the toluenesulphonyl group only was eliminated; the final products were violet-blue dyes, very stable to alkalis and light. F. M. G. M.

Hyposulphites. VII. Rongalite and Salts of Amines. ARTHUR BINZ and TH. MARX (*Ber.*, 1910, **43**, 2344—2349. Compare Binz and Isaac, Abstr., 1908, i, 940).—The hydrochlorides of amines react with rongalite even in the absence of formaldehyde. It is suggested that the hydrochloride first condenses with the sodium salt according to the equation

$$RNH_2,HCl + OH\cdot CH_2\cdot O\cdot S\cdot ONa = RNH\cdot CH_2\cdot O\cdot S\cdot OH + NaCl + H_2O,$$

and that the substituted formaldehydesulphoxylic acid then forms a salt with the excess of the amine hydrochloride:

$$RNH\cdot CH_2\cdot O\cdot S\cdot OH + RNH_2,HCl = RNH\cdot CH_2\cdot O\cdot S\cdot O\cdot NH_3R + HCl,$$

and that it is this salt which is precipitated. In the case of ammonium chloride and of hydroxylamine hydrochloride, it has been found possible to isolate the intermediate product. The salts are decomposed by cold dilute sodium hydroxide solution, and practically half the amine used up in the formation of the compound is liberated.

Rongalite and *o*-toluidine hydrochloride yield the salt

$$C_6H_4Me\cdot NH\cdot CH_2\cdot O\cdot SO\cdot NH_3\cdot C_6H_4Me$$

in the form of colourless crystals, m. p. 101—104°. It turns a yellow colour on exposure to the air, and reduces warm indigocarmin solution. When an excess of rongalite is used, mixtures are formed.

Rongalite and anthranilic acid hydrochloride yield colourless crystals of the compound $C_{15}H_{16}O_6N_2S$, m. p. 143° (decomp.). When diazotised, it yields salicylic acid, and when oxidised with hydrogen peroxide or with sodium thiosulphate yields anthranilic acid. Rongalite and hydroxylamine hydrochloride in the presence of formaldehyde solution yield *hydroxylaminomethylsulphurous acid*, $OH\cdot NH\cdot CH_2\cdot O\cdot SO_2H$, owing to the oxidising action of the hydroxylamine. It can be crystallised from water, does not reduce indigocarmin, and has m. p. 191°. J. J. S.

Preparation of Thiodiphenylamine and its Derivatives. FRITZ ACKERMANN (D.R.-P. 224348).—The preparation of thiodiphenylamines with the aid of sulphur and aluminium chloride has previously been described; it is now found that aluminium bromide or iodide, ferric chloride, antimony trichloride, cuprous iodide, sulphur iodide, or iodine can be employed equally well, and the methods of doing so with their extension to the preparation of thio-β-dinaphthylamine and thiophenyl-β-naphthylamine are described. *Thio-*p*-tolyl-β-naphthylamine* was obtained as a greenish-yellow powder, m. p. 182°. F. M. G. M.

Action of Magnesium Alkyl Halides on Anilides and their Chlorides. MAX BUSCH and MARTIN FLEISCHMANN (*Ber.*, 1910, **43**, 2553—2556)—Béis has shown that the interaction of acid amides

and magnesium alkyl halides leads to the formation of ketones and ammonia (Abstr., 1904, i, 15). When the aminic hydrogen atoms are replaced by alkyl groups, the authors find that a dual reaction occurs; thus, magnesium phenyl bromide (2 mols.) and benzoylethylaniline in ether yield ultimately benzophenone and ethylaniline (from $OMgBr\cdot CPh_2\cdot NEtPh$), and also *triphenylmethylethylaniline*,

$$CPh_3\cdot NEtPh,$$

m. p. 92° (from $OMgBr\cdot CPh_2\cdot NEtPh$ and PhMgBr), which easily decomposes in alcoholic solution into triphenylcarbinol and ethylaniline.

Magnesium alkyl halides react with imino-chlorides generally either at the double linking or at the reactive halogen atom, yielding the same product in both cases, but sometimes at both of these points of attack. Thus benzanilideimino-chloride and ethereal magnesium methyl iodide yield ultimately acetophenoneanil, $NPh\text{:}CPhMe$, which cannot be isolated, but the presence of which is proved by hydrolysis with hydrochloric acid, whereby acetophenone and aniline are obtained. In a similar way the imino chloride reacts with magnesium ethyl bromide to form ultimately an anil which yields aniline and phenyl ethyl ketone by hydrolysis, and with magnesium phenyl bromide to form ultimately benzophenoneanil, m. p. 113—114°; once in the latter preparation a considerable amount of triphenylmethylaniline, $CPh_3\cdot NHPh$, was obtained, but the conditions of its formation could not be repeated. C. S.

Metathetical Reactions: Ether-thiocarbamides and their Relation to ψ-Ammonium Bases. TREAT B. JOHNSON and HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1910, **32**, 1279—1285).—Cyclic quaternary bases (pyridines, quinolines, *iso*quinolines, and acridines) undergo isomeric change in aqueous solution, the hydroxyl group of the base migrating from the nitrogen to a carbon atom with formation of ψ-ammonium bases. The latter compounds react with alcohols at the ordinary temperature with loss of a molecule of water and production of alcoholates or ethers. When these alcoholates are warmed with alcohols, the alkyl group of the alcoholate is replaced by that of the alcohol. The mechanism of this change has been interpreted in different ways (compare Decker, Abstr., 1900, i, 522, and Gadamer, Abstr., 1905, i, 368; 1908, i, 322). In order to throw further light on these transformations, a study has been made of some ether-thiocarbamides.

The ether-thiocarbamides, $OR\cdot CH_2\cdot NH\cdot CS\cdot NHR'$, were obtained by the action of certain thiocarbimidomethyl ethers, $RO\cdot CH_2\cdot NCS$, on organic bases (Johnson and Guest, Abstr., 1909, i, 371). These substances are closely related to the cyclic alcoholates, as they contain the same complex, $\text{:}\underset{|}{C}\cdot\underset{|}{N}\cdot\underset{|}{C}H\cdot OR$, and hence may be regarded as acyclic ψ-ammonium compounds. The ether-thiocarbamides would therefore be expected to undergo transformations with alcohols analogous to those which take place with the cyclic alcoholates, and such has been found to be the case. All the ether-thiocarbamides which have been examined react with alcohols on warming, with transposition of the alkyl groups. These reactions are reversible, and are not affected by

the b. p.'s of the alcohols or by the size of the alkyl groups involved. It is therefore possible to obtain a whole series of ether-thiocarbamides from one thiocarbimidomethyl ether. These transformations are most easily explained by assuming that unstable additive compounds are first formed, and that these decomposes with production of a new thiocarbamide and alcohol.

s-*Phenylmethoxymethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot OMe$, m. p. 133°, obtained by recrystallising *s*-phenylethoxymethylthiocarbamide or *s*-phenyl*iso*amyloxymethylthiocarbamide from methyl alcohol, forms prismatic crystals. s-p-*Tolylmethoxymethylthiocarbamide*,

$$C_6H_4Me\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot OMe,$$

m. p. 129°, is obtained by the action of methyl alcohol on the corresponding ethoxy-compound. E. G.

Replacement of Halogen by the Nitro-group. II. L. CHAS. RAIFORD and FREDERICK W. HEYL (*Amer. Chem. J.*, 1910, **44**, 209—219).—It has been found previously (this vol., i, 373) that when 2 : 4 : 6-tribromophenol is treated with nitrous acid, a mixture of 4 : 6-dibromo-2-nitrophenol and 2 : 6-dibromo-4-nitrophenol is produced, but that 2 : 4 : 6-trichlorophenol is not affected by nitrous acid. In view of these results, it was considered of interest to study the behaviour of 2 : 4 : 6-tri-iodophenol. The work has also been extended to 2 : 4 : 6-tribromoresorcinol.

2 : 4 : 6-Tri-iodophenol has m. p. 158°, instead of 156°, as stated by Messinger and Vortmann (Abstr., 1889, 1150). The *acetate*, m. p. 154°, forms colourless needles. When sodium nitrite is added gradually to a solution of 2 : 4 : 6-tri-iodophenol in a mixture of glacial acetic acid and benzene at 12—15°, 4 : 6-di-iodo-2-nitrophenol is obtained, together with 2 : 6-*di-iodo-4-nitrophenol*, m. p. 155°, which forms nearly colourless prisms. It is probable that a small quantity of an iododinitrophenol is also produced in this reaction. On reducing 4 : 6-di-iodo-2-nitrophenol with stannous chloride in presence of hydrochloric acid, the *hydrochloride* of 4 : 6-di-iodo-2-aminophenol is obtained, which crystallises in long prisms.

When a solution of 2 : 4 : 6-tribromoresorcinol in glacial acetic acid is treated with sodium nitrite at 12—15°, 2 : 6-*dibromo-4-nitroresorcinol*, m. p. 148°, is produced, which forms maroon prisms or orange needles; its *ammonium* salt crystallises in deep yellow prisms. On reducing this nitro-compound with a solution of stannous chloride in hydrochloric acid, the *hydrochloride* of 2 : 6-*dibromo-4-aminoresorcinol* is obtained. 2 : 6-*Dibromo-4-aminoresorcinol* darkens above 135°, and decomposes above 175° without melting; it crystallises in prisms which are at first colourless, but soon become grey; the *picrate* begins to decompose at 220° without melting. 2 : 6-*Dibromo-4-acetylaminoresorcinyl diacetate*, m. p. 174—175°, forms colourless, hexagonal plates.

E. G.

Preparation of *o*- and *p*-Nitrophenols. R. S. HART (*J. Amer. Chem. Soc.*, 1910, **32**, 1105—1106).—Phenol (50 grams) dissolved in alcohol (5 grams) is added drop by drop (30 drops a minute) to a solution of sodium nitrate (80 grams) in sulphuric acid (100 grams) diluted with 200 c.c. of water at 25°. The mixture is stirred vigorously

during the addition, and for half an hour afterwards. After an hour and a-half, the liquid is treated in the usual way, and gives a yield of 30 grams of *o*-nitrophenol and 13 grams of *p*-nitrophenol. W. O. W.

Phenyl Ether and Some of its Derivatives. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1910, **32**, 1285—1294).—The ethers used in this investigation were prepared by distilling the aluminium derivatives of the corresponding phenols. Good yields were obtained of phenyl and *m*-tolyl ethers, but only small yields of *o*- and *p*-tolyl ethers. On rapidly distilling aluminium *p*-tolyloxide, flashes appeared on the surface of the liquid. When some aluminium *p*-tolyloxide which had been exposed to the air for about two months was distilled, *p*-cresol was obtained, but very little *p*-tolyl ether. The causes of these phenomena are being investigated.

Tetrabromophenyl ether, $O(C_6H_3Br_2)_2$, b. p. 280—290°/25 mm., 410—425°/760 mm., m. p. 83—84°, prepared by slowly adding an excess of bromine to a solution of phenyl ether in carbon disulphide containing a little iodine to serve as a carrier, forms large needles. It was not found possible to obtain a more highly brominated derivative.

Dibromo-m-*tolyl ether*, $O(C_6H_3MeBr)_2$, b. p. about 250°/15 mm. and 340—350° (uncorr.)/760 mm., m. p. 48°, prepared by slowly adding the calculated quantity of bromine to a solution of *m*-tolyl ether in carbon disulphide, forms white crystals. *Tetrabromo*-m-*tolyl ether*, $O(C_6H_2MeBr_2)_2$, b. p. 260—270°/35 mm., is obtained by the action of an excess of bromine on *m*-tolyl ether in presence of a little iodine as a viscous substance which slowly crystallises. A more highly brominated derivative could not be obtained.

2 : 4-*Dinitrophenyl* p-*tolyl ether*, $C_6H_4Me{\cdot}O{\cdot}C_6H_3(NO_2)_2$, m. p. 93°, prepared by the action of potassium *p*-tolyloxide on 1-bromo-2 : 4-dinitrobenzene, forms yellow crystals. The *sulphonic acid*,

$$SO_3H{\cdot}C_6H_3Me{\cdot}O{\cdot}C_6H_3(NO_2)_2,$$

m. p. 150° (decomp.), crystallises in slender needles containing $1\frac{1}{2}H_2O$; its *barium* and *sodium* salts are described. When a solution of 2 : 4-dinitrophenyl *p*-tolyl ether in glacial acetic acid is warmed with chromic anhydride, it is converted into p-2 : 4-*dinitrophenoxybenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_3(NO_2)_2$, a yellow substance which does not melt below 200°; its *silver* salt is described.

2 : 4-*Dinitrophenyl ether*, $C_6H_5{\cdot}O{\cdot}C_6H_3(NO_2)_2$, m. p. 70°, b. p. 230—250°/27 mm.; obtained by the action of potassium phenoxide on 1-bromo-2 : 4-dinitrobenzene, is a crystalline substance with a faint odour and a pungent taste. The *sulphonic acid*, $SO_3H{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_3(NO_2)_2$, forms white, pearly flakes; its *barium* salt is described. *Trinitrophenyl ether*, $C_{12}H_7O(NO_2)_3$, prepared by dissolving 2 : 4-dinitrophenyl ether in concentrated nitric acid, crystallises in clusters of yellow prisms.

A bibliography of phenyl ether and its derivatives is appended.

E. G.

Organic Compounds of Quadrivalent Tellurium. CHARLES LEDERER (*Compt. rend.*, 1910, **151**, 611—612).—Tellurium tetrachloride (1 mol.) reacts with magnesium phenyl bromide (5 mols.) in

dry ether. In addition to chlorobenzene, diphenyl, and diphenyl telluride, the product yields a sparingly soluble material when treated with a limited amount of water. On treatment with aqueous potassium iodide this furnishes *diphenyltellurium di-iodide*, decomposing at 236—237°, and *triphenyltelluronium iodide*, $TePh_3I$. The latter crystallises in colourless needles, m. p. 247—248°, and on treatment with silver chloride or bromide gives the corresponding *chloride*, m. p. 244—245° (decomp.), and *bromide*, m. p. 259—260°.

Fixation of hydrogen chloride by diphenyltellurium leads to the formation of the *compound*, $TeHPh_2Cl$, m. p. 233—234°. W. O. W.

Preparation of Neutral Phenolic Esters of Diglycollic Acid. C. F. BOEHRINGER & SÖHNE (D.R.-P. 223305).—The phenyl esters of diglycollic acid are readily prepared by treating the acid dichloride with the required phenol or sodium phenoxide (substituted or otherwise) in the presence of an indifferent base, such as dimethylaniline.

Diphenyl diglycollate, $O(CH_2{\cdot}CO_2Ph)_2$, forms colourless needles, m. p. 80°.

Disalicyl diglycollate forms colourless crystals, m. p. 173°; the *a-naphthyl* ester, colourless leaflets, m. p. 136°; the *β-naphthyl* ester, a colourless, crystalline powder, m. p. 160°; the *guaiacol* ester, colourless needles, m. p. 82°; the o-*tolyl* ester, needles, m. p. 101°; the m-*tolyl* ester, needles, m. p. 63°; the p-*tolyl* ester, needles, m. p. 89°; the o-*chlorophenyl* ester, needles, m. p. 129°; the p-*chlorophenyl* ester, slender needles, m. p. 130°; the o-*nitrophenyl* ester, colourless leaflets, m. p. 164°, and the p-*nitrophenyl* ester, a colourless, crystalline powder, m. p. 131°.

The solubility of these compounds in numerous solvents is fully described in the patent. F. M. G. M.

[Simple Formation of Benzyl Ethers.] JULIUS VON BRAUN (*Ber.*, 1910, **43**, 2594).—Reply to Halban (this vol., i, 619). C. S.

The Addition of Bromine to Unsaturated Compounds. I. Allyl and Propenyl Derivatives of Benzene. GINO ABATI (*Gazzetta*, 1910, **40**, ii, 89—94. Compare Abstr., 1909, i, 104).—A comparison of the velocity of addition of bromine in chloroform solution to chavicol and anethole, eugenol and *iso*eugenol and their methyl derivatives, safrole and *iso*safrole, myristicin and *iso*myristicin, and apiole and *iso*apiole, show that the velocity is always greater in the case of the propenyl derivative.

The molecular refractive indices of myristicin and *iso*myristicin have also been measured, and are found to be M_α 89·44 and M_α 92·94 respectively. C. H. D.

The Xylenol from Dehydracetic Acid. EMILIO CARLINFANTI and A. GERMAIN (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 234—239).—The xylenol produced when dehydracetic acid is distilled with calcium oxide is not *o*-4-xylenol, as stated by Tivoli (Abstr., 1891, 1455), but the 1:3:5-compound. The mistake is due to the fact that a substance is also formed which gives a reaction

with ferric chloride similar to that of *o*-4-xylenol, and this impurity can only be removed by repeated crystallisation. When calcium acetate is heated with calcium oxide, a yellow *oil*, b. p. 215—225°, is obtained, which has no phenolic properties, but gives an intense coloration with ferric chloride. To explain the formation of *m*-5-xylenol, the following mechanism is suggested. Dehydracetic acid under the conditions of the experiment yields acetyltriacetic acid, which loses carbon dioxide and is converted into diacetylacetone, which decomposes into acetic acid and acetylacetone; this then condenses with the acetone formed from the calcium acetate. In confirmation of this view, the authors find that *m*-5-xylenol is produced when a mixture of the vapours of these two substances is led over calcium oxide at 400°.

5-*Hydroxy*-m-*xylyl phenylcarbamate*, $C_8H_9O\cdot CO\cdot NHPh$, crystallises in shining needles, m. p. 148—149°. R. V. S.

Fluorenyl Ethers. ALFRED KLIEGEL (*Ber.*, 1910, **43**, 2488—2496. Compare Abstr., 1905, i, 187).—Schmidt and Stützel (this vol., i, 29) on reducing fluorenoneoxime by tin and hot concentrated hydrochloric acid obtained fluorenyl ether, possessing a red colour, and quite different from the fluorenyl ether obtained by Barbier from fluorenyl alcohol. This red compound, the colour of which was attributed to the accumulation of benzene nuclei, is not in agreement with Witt's theory of colour.

By the action of silver oxide on 9-chlorofluorene, fluorenyl ether was obtained in colourless, lustrous plates, m. p. 228°, and it is further shown that the red compound of Schmidt and Stützel is in reality diphenylene-phenanthrone, m.p. 257°, coloured red by admixture with di-biphenylene ethylene, m. p. 187°.

The first product of the action of hydrochloric acid and tin, or, better, of stannous chloride, is a glistening, red, crystalline compound, which is a *stannichloride* of 9-*iminofluorene*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C\!:\!NH$. The *picrate* crystallises in lustrous, orange needles, and when decomposed with ammonia yields the crystalline base, which separates in pale straw-yellow, slender needles, m. p. 124°. On warming with water, it readily decomposes into ammonia and ketone. An egg-yellow and an orange *oxalate* and a similarly coloured *sulphate* were also isolated. The *acetate* crystallises in citron-yellow needles, m. p. 104°. E. F. A.

[*m*-Hydroxyphenyl Mercaptan.] LADISLAUS VON SZATHMÁRY (*Ber.*, 1910, **43**, 2485—2487).—Sodium *m*-benzenedisulphonate was converted into sodium *m*-phenolsulphonate, and this into the *sulphonyl chloride*, which was obtained as a viscid, oily, brown product having a pungent, disagreeable odour. It is reduced by tin and hydrochloric acid to m-*hydroxyphenyl mercaptan*. This crystallises when strongly cooled, but is oily at the ordinary temperature. It has a pungent, unpleasant odour, and with lead acetate yields an insoluble, stable, yellow precipitate of the *lead* salt, $Pb(S\cdot C_6H_4\cdot OH)_2$. It shows no coloration with either sulphuric acid or sodium hydroxide. E. F. A.

Symmetrical Trithiophenols. JACQUES POLLAK and R. TUCAKOVIĆ (*Monatsh.*, 1910, **31**, 695—707).—*Trithiomethylphloroglucinol* [*toluene-2 : 4 : 6-trithiol*], $C_6H_2Me(SH)_3$, prepared by reducing *o*-tolyl-2 : 4 : 6-trisulphonyl chloride with tin and hydrochloric acid, forms white needles, m. p. 49—53°, having a characteristic odour. It readily undergoes oxidation, either on exposure to the air or under the action of oxidising agents, with the formation of yellow to yellowish-red products. With lead acetate, it gives a yellow precipitate, which quickly changes to red. In glacial acetic acid solution, it is readily transformed into the original trisulphonyl chloride by the action of chlorine.

The *triacetyl* derivative, $C_6H_2Me(SAc)_3$, forms needles, m. p. 93—95°, and is readily obtained by heating with acetic anhydride and fused sodium acetate. The *trimethyl ether*, $C_{10}H_{14}S_3$, prepared by the action of diazomethane in ethereal solution, or of methyl iodide in alkaline alcoholic solution, forms slender needles, m. p. 61—63°; it cannot be obtained by the action of hydrogen chloride and methyl alcohol. Trithiomethylphloroglucinol consequently behaves as a non-tautomeric phenol.

The condensation product with chloroacetic acid,

$$C_6H_2Me(S\cdot CH_2\cdot CO_2H)_3,$$

has m. p. 197—200°; the *ethyl* ester, $C_6H_2Me(S\cdot CH_2\cdot CO_2Et)_3$, has m. p. 30—35°.

The action of cold concentrated nitric acid (D 1·4) on the trimethyl ether gives rise to the *mononitro*-derivative, $NO_2\cdot C_6HMe(SMe)_3$, yellow prisms, m. p. 84—87°. With hot concentrated nitric acid or cold fuming nitric acid, a *monosulphoxide* of the above-mentioned nitro-derivative is produced, $NO_2\cdot C_6HMe\cdot(SMe)_2\cdot SOMe$, which forms slender, yellow needles, m. p. 178·5—179·5°. The position of the sulphoxide group has not been ascertained. Hot fuming nitric acid also gives rise to a substance, m. p. 235—237°, which requires further investigation.

Trithiophloroglucinol (Abstr., 1909, i, 761) has now been obtained in the form of white needles, m. p. 57—60°. The product,

$$C_6H_3(S\cdot CH_2\cdot CO_2H)_3,$$

obtained with chloroacetic acid forms white, silky needles, m. p. 179—180°, from which the *ethyl* ester was obtained as an oil. The trimethyl ether gives the *mononitro*-derivative, $NO_2\cdot C_6H_2(SMe)_3$, with cold concentrated nitric acid; it forms dark yellow, slender needles, m. p. 148—150°. T. S. P.

Cholesterol. II. LEO TSCHUGAEFF and W. FOMIN (*Annalen*, 1910, **375**, 288—297. Compare this vol., i, 31, 479).—In addition to work already recorded, the paper contains the following results. *Ethyl cholesterylxanthate*, $C_{27}H_{45}O\cdot CS\cdot SEt$, m. p. 141·5°, and the *propyl* ester, m. p. 135°, have almost the same dispersion coefficient as the methyl ester. *Cholesterylxanthamide*, $C_{27}H_{45}O\cdot CS\cdot NH_2$, m. p. 227°, is obtained by digesting the methyl ester with about 10% alcoholic ammonia for many days.

The constitutions of *a*-cholesterylene, cholesterol, *β*-cholesterylene,

and cholestane are represented respectively by: $R<^{CH}_{CH_2}>CH$, $R<^{CH_2}_{CH_2}>CH\cdot OH$, $R<^{CH_2}_{CH}>CH$, and $R<^{CH_2}_{CH_2}>CH_2$, where R is $^{CH_2Pr^{\beta}\cdot CH_2}_{CH_2:CH}>C_{17}H_{26}$.

C. S.

Aromatic Fluorine Derivatives and Estimation of Fluorine in the Same. HANS MEYER and ALFRED HUB (*Monatsh.*, 1910, **31**, 933—938).—The three fluorobenzoic acids can be prepared readily by the oxidation of the fluorotoluenes with permanganate (compare Hollemann, Abstr., 1905, i, 425). The *o*-acid has m. p. 122°. The corresponding fluorobenzoyl chlorides, $C_6H_4F\cdot COCl$, can be obtained by the action of thionyl chloride on the acids. They are colourless, strongly refractive liquids with an odour resembling that of benzoyl chloride. The *o*-compound has b. p. 204° and m. p. 4°; the *m*-compound, b. p. 189° and m. p. −30°, and the *p*-compound, b. p. 191—192° and m. p. 9°.

The *methyl* esters, $C_6H_4F\cdot CO_2Me$, have boiling points and melting points as follows: ortho, 207°, −20°; meta, 194—195°, −10°, and para, 197°, 4·5°. Some of these compounds have lower b. p.'s than the unsubstituted derivatives.

o-*Fluorobenzamide*, $C_6H_4F\cdot CO\cdot NH_2$, crystallises from water in colourless needles, m. p. 114°; the *meta*-compound in colourless plates, m. p. 128—129°, and the *para*-compound in colourless needles, m. p. 153°.

In estimating the fluorine in these compounds, the substance is heated with lime in a nickel tube, 40 cm. long and 4—5 mm. diameter, the end of which is closed by means of silver solder. The tube is treated in much the same manner as in the estimation of halogens by the lime method; it is necessary, however, to see that the lime is completely soluble in dilute acetic acid, and a temperature of 1000° must be attained in all parts of the tube. At the end the calcium fluoride is estimated in the usual manner. J. J. S.

Condensation Products of Anthranilic Acid with Aromatic Aldehydes. HUGO WOLF (*Monatsh.*, 1910, **31**, 903—916).—Various aromatic aldehydes have been condensed with anthranilic acid in alcoholic solution in order to determine whether the resulting Schiff's bases exist in stereoisomeric forms (compare Hantzsch and Schwab, Abstr., 1901, i, 378; Anselmino, *ibid.*, 1907, i, 913; Manchot and Furlong, *ibid.*, 1909, i, 805; this vol., i, 33).

Two isomeric forms were observed in the anils obtained by the condensation of the acid with *o*- and *p*-hydroxybenzaldehydes.

Benzylideneanthranilic acid, $CHPh:N\cdot C_6H_4\cdot CO_2H$, crystallises in sulphur-yellow needles, m. p. 128°; p-*tolylideneanthranilic acid*, $C_6H_4Me\cdot CH:N\cdot C_6H_4\cdot CO_2H$, forms lemon-yellow, rectangular plates, m. p. 154°; o-*nitrobenzylideneanthranilic acid*,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

crystallises in yellow needles, m. p. 172°, and readily turns red on

exposure to the air; the isomeric *para*-compound forms pale yellow plates, m. p. 162°, and the *meta*-derivative, pale yellow needles, m. p. 206°.

Salicylideneanthranilic acid, $OH\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H$, separates as small, yellow plates, m. p. 193°, when its alcoholic solution is cooled rapidly, otherwise the red modification, which crystallises in stout prisms, m. p. 200°, is obtained. The yellow crystals are transformed into the red when dissolved in amyl alcohol and the solution cooled slowly, or when the solution is cooled quickly and the yellow crystals left in contact with the amyl alcohol mother liquor for several hours. p-*Hydroxybenzylideneanthranilic acid* exists in yellow and red modifications, of which the red is the less stable. The yellow form is more readily soluble in ether than the red, and has m. p. 224°. The isomeric m-*hydroxy*-derivative crystallises in yellow prisms, m. p. 182°.

o-*Methoxybenzylideneanthranilic acid*, $OMe\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H$, forms yellow needles, m. p. 128°; the isomeric *para*-compound crystallises in yellow, rectangular plates, m. p. 142°, which turn red on exposure to the air. *Dimethylaminobenzylideneanthranilic acid*,

$$NMe_2\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

forms brick-red prisms, m. p. 214°.

3 : 4-*Dihydroxybenzylideneanthranilic acid*,

$$C_6H_3(OH)_2\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

crystallises in glistening, red needles, m. p. 226° (decomp.). 4-*Hydroxy-3-methoxybenzylideneanthranilic acid*,

$$OMe\cdot C_6H_3(OH)\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

forms slender, lemon-yellow needles, m. p. 164°. 3 : 4-*Piperonylideneanthranilic acid*, $CH_2O_2:C_6H_3\cdot CH:N\cdot C_6H_4\cdot CO_2H$, forms pale yellow, rectangular plates, m. p. 188°. *Cinnamylideneanthranilic acid*, $CHPh:CH\cdot CH:N\cdot C_6H_4\cdot CO_2H$, crystallises from toluene or ethyl acetate in yellow prisms, m. p. 156°. When heated at 100°, it begins to turn red, and gives an odour of cinnamaldehyde.

When alcoholic solutions of these anil acids are heated with the equivalent amount of phenylhydrazine for about thirty minutes on the water-bath, the $:N\cdot C_6H_4\cdot CO_2H$ group is replaced by the

$$:N\cdot NHPh$$

group, and the phenylhydrazones of the aldehydes are obtained.

J. J. S.

Lactonoid Anhydrides of Acylated Amino-acids. V. Lactone of *r*-Benzoylphenylalanine. ERNST MOHR and FR. STROSCHEIN (*J. pr. Chem.*, 1910, [ii], **82**, 322—335. Compare this vol., i, 483, 557).—Much of the work has been recorded (Abstr., 1909, i, 581). The ethyl ester, chloride, and amide of benzoylphenylalanine (Max, Abstr., 1909, i, 926) are conveniently prepared from the lactone; also the *anilide*, $CH_2Ph\cdot CH(NHBz)\cdot CO\cdot NHPh$, m. p. 233—234°, from the lactone and aniline in dry ether. *Benzoylphenylalanylglycine*, $CH_2Ph\cdot CH(NHBz)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 240—242° (decomp., softening at 185°), is obtained from glycine and the lactone of benzoylphenylalanine at 130°, or, better, in aqueous acetone in the presence of sodium hydroxide.

C. S.

o-Aminobenzyl Cyanide [o-Aminophenylacetonitrile] and its Conversion into 2-Aminoindole and Indole. ROBERT PSCHORR and GERH. HOPPE (*Ber.*, 1910, **43**, 2543—2552).—The conversion of *o*-aminocinnamonitrile into 2-aminoquinoline by acids or alkalis (Pschorr, Abstr., 1898, i, 491) induced the authors to examine the behaviour of *o*-aminophenylacetonitrile under similar conditions. This substance is conveniently prepared by converting *o*-nitrophenylacetic acid by a suspension of phosphorus pentachloride in ether into the chloride, a solution of which in benzene and ether is converted by ammonia into o-*nitrophenylacetamide*, m. p. 160°; the amide is converted by thionyl chloride into the nitrile, an alcoholic solution of which is reduced by stannous chloride and concentrated hydrochloric acid to o-*aminophenylacetonitrile*, m. p. 72°, which is best isolated by treating an aqueous solution of its stannichloride with 30% sodium hydroxide, whereby the substance separates in almost quantitative yield. The presence of the "activated" methylene group in the ortho-position to the amino-group renders derivatives of the substance very liable to intramolecular condensation. Thus a solution of *o*-aminophenylacetonitrile in *N*-hydrochloric acid is converted into *indazolecarboxylonitrile*, $C_6H_4<\genfrac{}{}{0pt}{}{C(CN)}{N\text{———}}>NH$, m. p. 140°, whilst a solution in ether yields by treatment with sodium and amyl formate, *indole-3-carboxylonitrile*, m. p. 178°. This nitrile forms an *acetyl* derivative, m. p. 202°, which is also obtained when *indole-3-aldoxime*, m. p. 197—200°, is heated with acetic anhydride.

o-Aminophenylacetonitrile yields a *formyl* derivative,

$$CN\cdot CH_2\cdot C_6H_4\cdot NH\cdot CHO,$$

m. p. 110°, which shows no tendency to intramolecular condensation, and is simultaneously hydrolysed and converted into 2-aminoindole by boiling potassium carbonate; an *acetyl* derivative, m. p. 120°, and a *diacetyl* derivative, m. p. 80°.

By treatment with boiling alcoholic sodium ethoxide in an atmosphere of hydrogen, *o*-aminophenylacetonitrile is converted into 2-*aminoindole*, $C_6H_4<\genfrac{}{}{0pt}{}{CH}{NH}>C\cdot NH_2$, which separates from water in prisms containing H_2O, has a strongly alkaline reaction, is reduced by sodium and alcohol to indole, and forms a *diacetyl* derivative, m. p. 142°, which is converted by aqueous potassium carbonate into 2-*acetylaminoindole*, m. p. 167°. When an ethereal solution of 2-aminoindole is treated with ethyl chloroformate, three products are obtained, two of which, m. p. 93° and 160° respectively, are isomeric and contain two carbethoxy-groups, whilst the third has m. p. 145—150° and contains only one carbethoxy-group. The constitution of 2-aminoindole is proved by the fact that Piccini and Salmoni's indole-2-urethane, by treatment with ethyl chloroformate, yields the isomeride, m. p. 93°, containing two carbethoxy-groups, mentioned above. C. S.

Action of Thionyl Chloride on Benzilic Acid. ROBERT STOLLÉ (*Ber.*, 1910, **43**, 2471—2473).—By the interaction of thionyl chloride and benzilic acid in carbon tetrachloride solution at the ordinary temperature, α-chlorodiphenylacetic acid is formed. When the con-

stituents are boiled some days in the same solvent, *a-chlorodiphenylacetic anhydride*, $(CPh_2Cl\cdot CO)_2O$, is formed, m. p. 129°. This compound also arises when a-chlorodiphenylacetic acid is warmed with thionyl chloride. With aniline in ethereal solution, a-anilinodiphenylacetic acid, m. p. 168°, and *a-anilinodiphenylacetic anhydride*, crystallising in minute needles, m. p. 181°, and insoluble in sodium hydroxide, are formed.

A by-product of the action of thionyl chloride on benzilic acid crystallises in compact crystals insoluble in sodium carbonate, m. p. 119°. This is possibly *tetraphenyldiglycollyl chloride*, $C_{28}H_{30}O_3Cl_2$; it forms an anilide, m. p. 134°.

On shaking chlorodiphenylacetic anhydride in ether with sodium carbonate, an amorphous compound, probably benzilic anhydride, m. p. about 90°, is obtained. When heated with yellow mercuric oxide, chlorodiphenylacetic anhydride yields benzilide, m. p. 194°, which probably has the constitution of tetraphenyldiglycollic anhydride.

E. F. A.

Action of Dichloroacetic Acid on Aniline and its Homologues. III. GUSTAV HELLER with SALO ASCHKENASI (*Annalen*, 1910, **375**, 261—288. Compare Abstr., 1908, i, 216).—The paper contains a repetition of some of the earlier work in order to controvert Ostromisslensky's views of the course of the reaction between dichloroacetic acid and aniline or its homologues (Abstr., 1908, i, 82, 888, 889).

The reaction between dichloroacetic acid and *p*-anisidine furnishes the only case in which the initial product of the reaction has been isolated; *di*-p-*anisidinoacetic acid*, $CO_2H\cdot CH(NH\cdot C_6H_4\cdot OMe)_2$, m. p. 201—202°, forms a *hydrochloride*, $C_{16}H_{18}O_4N_2,HCl$, m. p. about 215°, cannot be diazotised or benzoylated, and does not form a nitrosoamine. The product of the reaction between dichloroacetic acid and *o*-toluidine is not *o*-methylaminophenyl-*o*-toluidinoacetic acid (Ostromisslensky, *loc. cit.*), but 2 : 2'-*diaminoditolyl*-4 : 4'-*acetic acid*,

$$CO_2H\cdot CH(C_6H_3Me\cdot NH_2)_2,$$

since it requires 2 mols. of sodium nitrite for diazotisation, and the diazotised product yields *bis-β-naphtholazodi*-o-*tolylacetic acid*,

$$C_{36}H_{28}O_4N_4,$$

m. p. 195°, *bis*-6-*sulpho-β-naphtholazodi*-o-*tolylacetic acid*,

$$C_{36}H_{28}O_{10}N_4S_2,$$

and *bis*-3 : 6-*disulpho-β-naphtholazodi*-o-*tolylacetic acid*,

$$C_{36}H_{28}O_{16}N_4S_4,$$

with β-naphthol, β-naphthol-6-sulphonic acid, and β-naphthol-3 : 6-disulphonic acid respectively. 2 : 2'-Diaminoditolyl-4 : 4'-acetic acid yields only a *monobenzoyl* derivative, m. p. 242—243°, by the Schotten-Baumann method; when benzoylated in the presence of sodium hydrogen carbonate, it yields a mixture of the preceding compound and an anhydro-derivative, $C_{23}H_{20}O_2N_2$, thereof.

2 : 2'-*Diamino-di*-m-*xylyl*-4 : 4'-*acetic acid*,

$$CO_2H\cdot CH(C_6H_2Me_2\cdot NH_2)_2,$$

m. p. 241°, obtained from aqueous potassium dichloroacetate, sodium acetate, and *m*-2-xylidine on the water-bath, or from an acetic acid solution of the base and glyoxylic acid at the ordinary temperature,

forms a *dibenzoyl* derivative, $C_{32}H_{30}O_4N_2$, m. p. 272° (decomp.), with benzoyl chloride in aqueous potassium hydroxide, an *anhydrobenzoyl* derivative, $C_{25}H_{24}O_2N_2$, unchanged at 300°, with benzoyl chloride in cold pyridine, and combines, after being diazotised, with β-naphthol-6-sulphonic acid in sodium carbonate solution to form a normal *bisazo-compound*, $C_{38}H_{32}O_{10}N_4S_2$, the combination in a solution of an alkali hydroxide yielding a black substance.

The usual reaction between dichloroacetic acid and ψ-cumidine yields 3-*ψ-cumidino*-4 : 5 : 7-*trimethyloxindole*,

$$C_6HMe_3<\begin{matrix}CH(NH\cdot C_6H_2Me_3)\\NH\text{———————}\end{matrix}>CO,$$

decomp. 205°; this is oxidised by iodine in glacial acetic acid to 4 : 5 : 7-*trimethylisatin*, $C_6HMe_3<\begin{matrix}CO\\NH\end{matrix}>CO$, m. p. 276°, which forms red needles, yields a *phenylhydrazone*, m. p. 248°, and is so stable to alkalis that the pyrrole nucleus is only ruptured at 50°.

The product of the direct action of dichloroacetic acid on aniline is not 4 : 4′-diaminodiphenylacetic acid (Ostromisslensky, *loc. cit.*), but its hydrochloride (Heller, Abstr., 1909, i, 20); the free acid has m. p. 195°, forms a *diacetyl* compound, m. p. 231°, and yields a *dibenzoyl* derivative, decomp. 256°, with benzoyl chloride and sodium hydroxide, and an *anhydrobenzoyl* derivative, $C_{21}H_{16}O_2N_2$, softening at 225°, with benzoyl chloride in cold pyridine. The product obtained by the addition of a dilute acetic acid solution of aniline to aqueous glyoxylic acid is aniline anilglyoxylate, not dianilinoacetic acid (Ostromisslensky, Abstr., 1908, i, 889), because only 1 mol. of aniline is eliminated by cold sodium carbonate. C. S.

Preparation of Oxyarylurethane Carbamido- and Thiocarbamido-cinnamic Acid Esters. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 224107).—Cinnamic acid esters of the general formula $C_6H_5\cdot CH\colon CH\cdot CO\cdot O\cdot R\cdot NH\cdot C<\begin{matrix}X\\Y\end{matrix}$ (where R is an aromatic radicle, X oxygen or sulphur, Y an alkyloxy-, amino-, or alkylamino-group) are readily prepared when cinnamoyl chloride is heated with *p*-hydroxyphenyl-carbamide or -urethanes; they are of great value in the treatment of tubercular complaints, and in surgery.

p-*Cinnamoyloxyphenylcarbamide*, colourless needles, m. p. 203°, is prepared by heating (or allowing to remain at the ordinary temperature) cinnamoyl chloride with *p*-hydroxyphenylcarbamide in aqueous alkaline solution.

m-*Cinnamoyloxyphenylcarbamide* has m. p. 204—205°.

p-*Cinnamoyloxyphenylurethane*, colourless needles, m. p. 150—151°, is prepared from the foregoing acid chloride and *p*-hydroxyphenylurethane, $OH\cdot C_6H_4\cdot NH\cdot CO_2Et$. o-*Cinnamoyloxyphenylurethane* has m. p. 101—102°.

p-*Cinnamoyloxyphenylallylcarbamide*,

$$CHPh\colon CH\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CS\cdot NH\cdot C_3H_5,$$

m. p. 129—130°, is prepared in analogous manner from *p*-hydroxyphenylallylthiocarbamide in acetone solution.

Cinnamic anhydride, or the acid in the presence of phosphoryl

chloride, can also be employed for this condensation, likewise other hydroxyphenylcarbamido-derivatives. F. M. G. M.

Melting Point of Granules of Salol. P. N. Pawloff (*Zeitsch. physikal. Chem.*, 1910, **74**, 562—566. Compare Abstr., 1908, ii, 927).—The relationship between the melting point of salol particles and their magnitude has been further investigated by heating commercial salol for long periods at constant temperatures, and determining by microscopic observation the surface area of the largest crystals which formed as a result of fusion and subsequent crystallisation. It was found necessary to heat for about two and a-half hours in order to obtain the maximum size of crystals.

The more fusible portion was investigated between 34·8° and 37·8° by the method described. The maximum crystal at 37·8° had a surface of 1296 sq. μ; the maximum formed at 34·8° a surface of 228 sq. μ. The less fusible portion was investigated between 39° and 41°. At the former temperature, particles of surface 200 sq. μ, at the latter temperature, particles of surface 1328 sq. μ, remain unaltered. The relative size of the crystals cannot readily be determined, but from the data obtained for the less fusible portion it is estimated that when the specific surface is increased one hundred times by dividing up the particles, the melting point is lowered by 2·8°. G. S.

Preparation of Monoiodosalicylic Acids or its Nuclear Homologues. Max Haase (D.R.-P. 224536. Compare Lassar-Cohn and Fritz Schultze, Abstr., 1905, i, 893).—The methods that have previously been employed for the preparation of monoiodosalicylic acids have given poor yields and impure products; the one now described is that whereby an alkaline solution of sodium salicylate is slowly treated with a very slight excess of iodine dissolved in potassium iodide at the ordinary temperature and with continual stirring; colourless needles, m. p. 197°, were obtained. Three iodosalicylic acids with m. p.'s 198°, 196°, and 199·5° have previously been described in the literature.
F. M. G. M.

Preparation of Amides of Monoiodosalicylic Acid and its Homologues. Max Haase (D.R.-P. 224346).—The amides of iodosalicylic acid (or other hydroxycarboxylic acids) can be readily prepared by treating the respective acid amide with potassium iodide and iodine in alkaline solution and allowing the mixture to remain at the ordinary temperature.

Iodosalicylamide, colourless leaflets, m. p. 230—231°, is sparingly soluble in hot water, and of therapeutic value. F. M. G. M.

Preparation of 5-Iodo-2-acetoxybenzoic Acid. Max Haase (D.R.-P. 224537).—The attempted preparation of iodoacetoxybenzoic acid from acetoxybenzoic acid results in the elimination of the acetyl group; it is now found that acetylation of iodosalicylic acid yields the required product.

5-*Iodo-2-acetoxybenzoic acid*, colourless needles, m. p. 175°, is prepared by boiling iodosalicylic acid with acetic anhydride in the presence

of anhydrous sodium acetate during three hours; it is a very important therapeutic agent, comparing favourably with *o*-acetoxybenzoic acid (aspirin) in being tasteless and less readily hydrolysed.

F. M. G. M.

Preparation of Acylsalicylic [*o*-Acyloxybenzoic] Anhydrides. ALFRED EINHORN (D.R.-P. 224844).—When the carbonyl esters of acylsalicylic acids (usually oils) having the general formula $OX\cdot C_6H_4\cdot CO\cdot O\cdot CO_2R$ (R = alkyl; X = acyl) are heated, they yield the corresponding crystalline acyl salicylic anhydride.

o-*Acetoxybenzoic anhydride*, glistening needles, m. p. 85°, is prepared by heating *o*-acetoxybenzoic acid with ethyl chlorocarbonate in benzene or ethereal solution in the presence of a tertiary base, such as pyridine; the *ethyl* o-*acetoxybenzoylcarbonate*, $OAc\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot OEt$, is isolated in the form of a viscid oil, which, when heated during ten to twenty-four hours on the water-bath, is transformed into the foregoing anhydride.

Benzoyloxybenzoic anhydride, prismatic needles, m. p. 109—111°, is similarly obtained from *ethyl* o-*benzoyloxybenzoylcarbonate*,

$$OBz\cdot C_6H_4\cdot CO\cdot O\cdot CO_2Et.$$

o-*Cinnamoyloxybenzoic acid anhydride*, slender needles, m. p. 110—112°, from *ethyl* o-*cinnamoyloxybenzoylcarbonate*, m. p. 53—55°. These compounds are of therapeutic value.

F. M. G. M.

The *N*-Methyl Derivatives of Phenylalanine and Tyrosine. ERNST FRIEDMANN and S. GUTMANN (*Biochem. Zeitsch.*, 1910, **27**, 491—497).—In connexion with earlier experiments on the behaviour of methylated amino-acids in the animal body (Friedheim, Abstr., 1908, ii, 205), the authors have prepared the methyl derivatives of the aromatic amino-acids occurring in proteins. α-*Methylamino*-β-*phenylpropionic acid* (*phenyl*-N-*methylalanine*), $CH_2Ph\cdot CH(NHMe)\cdot CO_2H$, prepared from aqueous methylamine and α-bromo-β-phenylpropionic acid, crystallises in three-sided plates subliming at 252—254° (decomp.).

p-*Methoxybenzylmalonic acid*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)_2$, prepared by reducing anisylidenemalonic acid with sodium amalgam by Knoevenagel's condensation, crystallises in large, irregular plates, m. p. 118·5° (decomp.). On treatment with bromine, it yields the α-*bromo*-derivative, $OMe\cdot C_6H_4\cdot CH_2\cdot CBr(CO_2H)_2$, which crystallises in four-sided leaflets decomposing at 153°. On heating at 120—130° with a little water, this gives α-*bromo*-β-p-*methoxyphenylpropionic acid*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CHBr\cdot CO_2H,$$

a brown, viscid oil, which with methylamine furnishes α-*methylamino*-β-p-*methoxyphenylpropionic acid*, crystallising in colourless scales, m. p. 256—257° (decomp.). This, on hydrolysis with hydrobromic acid, gives α-*methylamino*-β-p-*hydroxyphenylpropionic acid* (N-*methyltyrosine*), $OH\cdot C_6H_4\cdot CH_2\cdot CH(NHMe)\cdot CO_2H$, which crystallises in bunches of blunt needles, m. p. 318°.

G. S. W.

2-Naphthol-3-carboxylic Acid and its Condensation with Benzaldehyde. FRANZ FRIEDL (*Monatsh.*, 1910, **31**, 917—932. Compare J. Schmid, Abstr., 1893, i, 475; Möhlau, *ibid.*, 1896, i, 243).—The ketonic formula for 2-naphthol-3-carboxylic acid is some-

what analogous to that of benzyl methyl ketone; the condensation of benzaldehyde with methyl 2-naphthol-3-carboxylate in the presence of hydrogen chloride has been studied, and has been found to be of the same type as the condensation of benzyl methyl ketone and benzaldehyde in the presence of hydrogen chloride (Goldschmiedt and Krczmar, Abstr., 1901, i, 40), the resulting compound being methyl α-chloro-1-benzyl-2-naphthol-3-carboxylate, $C_6H_4<\begin{matrix} C(CHPhCl):C\cdot OH \\ CH{=\!=\!=}C\cdot CO_2Me \end{matrix}$, or the tautomeric ketone. The halogen atom in this compound is extremely reactive, and can be replaced readily by hydroxyl, methoxy-, phenoxy-, amino-, and anilino-groups (compare Braun, this vol., i, 479).

Methyl 2-naphthol-3-carboxylate has m. p. 73°.

Methyl α-chloro-1-benzyl-2-naphthol-3-carboxylate, $C_{19}H_{15}O_3Cl$, formed when dry hydrogen chloride is passed into a solution of methyl 2-naphthol-3-carboxylate in benzaldehyde at 0°, and the saturated solution kept for twenty-four hours, crystallises from perfectly dry benzene in microscopic prisms, m. p. 160—161°. At higher temperatures it loses hydrogen chloride, and at 220—225° is completely decomposed.

The corresponding *bromo*-derivative, $C_{19}H_{15}O_3Br$, has m. p. 183°; the hydroxy-derivative, *methyl 1-α-hydroxybenzyl-2-naphthol-3-carboxylate*, $C_{19}H_{16}O_4$, crystallises from benzene in pale yellow, glistening prisms, m. p. 173—174°. *Methyl 1 α-acetoxybenzyl-2-naphthol-3-carboxylate*, obtained by the action of acetic anhydride on the hydroxy-compound, forms pale yellow prisms, m. p. 136—137°. *Methyl α:2-diacetoxy-1-benzyl-3-naphthoate* has m. p. 70—73°, and decomposes at 85°. *Methyl 1-α-methoxybenzyl-2-naphthol-3-carboxylate*, $C_{20}H_{18}O_4$, prepared by the action of methyl alcohol on the chloro-derivative, crystallises from a mixture of benzene and alcohol in yellow, flat prisms, m. p. 177°. The corresponding *ethoxybenzyl* derivative, $C_{21}H_{20}O_4$, has m. p. 116—117°, and the *phenoxybenzyl* compound, $C_{25}H_{20}O_4$, m. p. 188°.

Methyl 1-α-aminobenzyl 2-naphthol-3-carboxylate, $C_{19}H_{17}O_3N$, crystallises from a mixture of chloroform and alcohol in yellow, microscopic prisms, m. p. 220°; the corresponding *anilinobenzyl* derivative, $C_{25}H_{21}O_3N$, crystallises in small prisms, m. p. 214°, and yields a *hydrochloride*, $C_{25}H_{21}O_3N,HCl$, in the form of colourless crystals, m. p. 175° (decomp.).

1-*Benzyl 2-naphthol-3-carboxylic acid*, $C_{18}H_{14}O_3$, obtained by heating the methyl ester of the chloro-acid with hydriodic acid, crystallises in lemon-yellow needles, m. p. 224°, and gives a blue coloration with ferric chloride; the *acetyl* derivative, $C_{20}H_{16}O_4$, forms colourless, glistening needles, m. p. 166°, and the *methyl* ester, $C_{19}H_{16}O_3$, microscopic, yellow needles, m. p. 107°.

Most of the compounds are probably equilibrium mixtures of the ketonic and enolic forms. J. J. S.

Condensation of Diphenyleneglycollic Acid with Phenols and Phenol Ethers. AUGUSTIN BISTRZYCKI and FRANZ VON WEBER (*Ber.*, 1910, 43, 2496—2505).—It was shown previously (Bistrzycki,

Abstr., 1901, i, 716) that benzilic acid condenses with phenols, and that the tertiary acids, formed readily on solution in concentrated sulphuric acid, lose carbon monoxide, forming carbinols: Diphenyleneglycollic acid likewise condenses with phenols, but the acids formed are only decomposed at high temperatures by concentrated sulphuric acid, and sulphonic acids of the expected carbinols are obtained.

9-p-*Hydroxyphenylfluorene-9-carboxylic acid*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > C(CO_2H) \cdot C_6H_4 \cdot OH,$$

prepared by condensation of diphenyleneglycollic acid with phenol, is obtained in microscopic, colourless, obliquely-cut plates from benzene containing a molecule of the solvent; it sinters and loses this at 98°, the residue becoming solid and getting red, m. p. 177° (decomp.). The benzene is difficult to remove; a preparation from alcohol had m. p. 178° (decomp.).

A by-product of the condensation is the *lactone* of 9-o-*hydroxyphenylfluorene-9-carboxylic acid*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > O < \begin{matrix} C_6H_4 \\ CO \end{matrix} > O$, which crystallises in microscopic, doubly refractive pyramids, m. p. 213°. On heating *p*-hydroxyphenylfluorenecarboxylic acid in a stream of air at 200°, carbon dioxide is eliminated, and 9-*p*-hydroxyphenylfluorene is formed, crystallising in colourless needles, m. p. 178—179° (decomp.), identical with the product obtained by Bistrzycki and Vlekke (*Diss.*, 1905) from phenol and fluorenyl alcohol.

9-p-*Acetoxyphenylfluorene*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > CH \cdot C_6H_4 \cdot OAc$, obtained on boiling *p*-hydroxyphenylfluorenecarboxylic acid with acetic anhydride, crystallises in slender needles, m. p. 139—140°.

9-p-*Hydroxy*-m-*tolylfluorene-9-carboxylic acid*, from diphenyleneglycollic acid and *o*-cresol, crystallises in matted prisms, m. p. 183—184° (decomp.). The corresponding *lactone* of 9-o-*hydroxy*-m-*tolylfluorene-9-carboxylic acid* separates in colourless plates, m. p. 147·5—149°.

9-p-*Hydroxy*-m-*tolylfluorene*, obtained by heating the above carboxylic acid at 220°, crystallises in colourless, six-sided prisms, m. p. 165—166° (decomp.). The *acetate* crystallises in rosettes of colourless prisms, m. p. 95—97°.

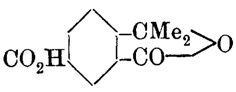
Diphenyleneglycollic acid condenses with *m*-cresol, forming a *p*-hydroxy-acid, which crystallises with difficulty. At the same time, 9-o-*hydroxy*-p(?)-*tolylfluorene-9-carboxylic acid lactone* is obtained; it separates in aggregates of obliquely-cut prisms, m. p. 192°. The *lactone* of 9-(2′-*hydroxy*-5′-*tolyl*)*fluorene-9-carboxylic acid* is the only product of the condensation with *p*-cresol. It is at first obtained as a red oil, and crystallises in transparent plates with many faces, m. p. 138°.

9-p-*Methoxyphenylfluorene-9-carboxylic acid*, prepared by condensation with anisole, forms a crust of colourless, microscopic plates, m. p. 144—145° (decomp.). 9-p-*Methoxyphenylfluorene*, obtained on heating the foregoing compound at 160°, forms colourless prisms, m. p. 121—122°.

E. F. A.

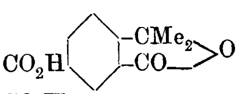
Synthesis of *iso*Propyl*iso*phthalic Acid and Dimethylphthalidecarboxylic Acid. GUIDO BARGELLINI (*Gazzetta*, 1910, 40, ii, 27—36).—The position assigned to the side-chain in santonin with respect to the ketonic group depends on the constitution of the dimethylphthalidecarboxylic acid obtained from it by Cannizzaro and Gucci (Abstr., 1893, i, 665). The acid has therefore been synthesised.

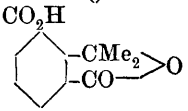
By nitrating cuminic acid with fuming nitric acid, 3-*nitrocuminic acid* (3-nitro-4-propylbenzoic acid) is obtained in prisms, m. p. 156—157°. Reduction with ammonium sulphide yields 3-*aminocuminic acid*, which crystallises in a labile modification, m. p. 104°, and a stable modification, m. p. 129°. Diazotisation, followed by heating with a solution of potassium copper cyanide, yields an uncrystallisable 3-cyanocuminic acid. This acid is very difficult to saponify, and it is necessary to convert it into the *amide*, $CO_2H\cdot C_6H_3Pr^{\beta}\cdot CO\cdot NH_2$, by boiling with sodium hydroxide. The product has m. p. 265°, and is



converted into *iso*propyl*iso*phthalic acid by dissolving in concentrated sulphuric acid and adding sodium nitrite. The product crystallises from boiling water, and has m. p. 236°. Oxidation with potassium permanganate in alkaline solution converts it into dimethylphthalidecarboxylic acid (annexed formula), which is identical with that prepared from santonin. C. H. D.

A New Synthesis of Dimethylphthalidecarboxylic Acid. GUIDO BARGELLINI and G. FORLÌ-FORTI (*Gazzetta*, 1910, 40, ii, 74—89. Compare preceding abstract).—An attempt has been made to prepare the acid (II) for comparison with the acid obtained from santonin, which is assumed to have the constitution (I). The method

I. 

II. 

selected was that of converting 3-nitrophthalic anhydride into the dimethylphthalide, and then of replacing the nitro-group by carboxyl. It is found, however, that the neighbourhood of the nitro-group prevents the anhydride from reacting with Grignard's reagent.

When dimethylphthalide is nitrated and the nitro-group replaced by carboxyl, an acid is obtained which is identical with that from santonin. The nitro-group is shown to occupy the para-position to the phthalide group, as it yields a nitrile which is readily saponified, whilst an *o*-nitrile would be difficult to saponify, as in the case of cyanocuminic acid. The nitration of methylphthalide (Giebe, Abstr., 1897, i, 63) and of diethylphthalide (Bauer, Abstr., 1904, i, 417; 1908, i, 274) is also known to yield para-derivatives. An attempt to prove the constitution directly by conversion into the hydroxy-compound, reduction, and distillation with lime, in order to examine the *iso*propylphenol produced, failed owing to the smallness of the yield obtained on reducing the hydroxyl compound with phosphorus and hydriodic acid.

The reduction of nitrodimethylphthalide with aluminium amalgam yields, instead of the amino-compound, an orange-yellow, crystalline

substance, m. p. 225—230°, devoid of basic properties. 5-*Amino-dimethylphthalide*, $NH_2\cdot C_6H_3<^{CMe_2}_{CO}>O$, obtained by reduction with stannous chloride, forms white leaflets, m. p. 117°. The *picrate* has m. p. 198—200°, softening at 192°. The *acetyl* derivative has m. p. 172—175°.

5-*Hydroxydimethylphthalide*, obtained by the diazo-reaction, forms white needles, m. p. 151—153°; its *acetyl* derivative has m. p. 76—78°; the *methyl ether* softens at 92—93° and melts at 98—99°.

In the attempt to prepare cyanodimethylphthalide by the diazo-reaction, an additive compound, m. p. 211—212°, is obtained, from which the compound may be isolated by heating in carbon dioxide, when cuminaldehyde volatilises, and a residue of 5-*cyanodimethylphthalide*, softening at 154° and melting at 159—160°, is obtained. Hydrolysis converts it into dimethylphthalidecarboxylic acid, identical with that obtained by other methods. C. H. D.

Retene. PAUL LUX (*Monatsh*, 1910, **31**, 939—949. Compare Bucher, this vol., i, 239).—Methyl*iso*propyldiphenamide,

$$NH_2\cdot CO\cdot C_6H_3Me\cdot C_6H_3Pr\cdot CO\cdot NH_2$$

(this vol., i, 239), crystallises from benzene, and has m. p. 204—206° (corr). When treated with bromine and potassium hydroxide solution, it yields 2 : 2′-*diamino*-3′-*methyl*-4-iso*propyldiphenyl*,

$$NH_2\cdot C_6H_3Me\cdot C_6H_3Pr^{\beta}\cdot NH_2,$$

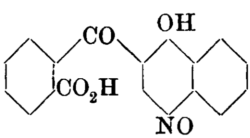
which forms colourless crystals, m. p. 89—90° (corr.). The *hydrochloride*, $C_{16}H_{20}N_2,2HCl$, melts above 240°. A better yield of the diamine can be obtained by using Jeffrey's method (Abstr., 1897, i, 315). The *urethane*, $CO_2Me\cdot NH\cdot C_6H_3Me\cdot C_6H_3Pr\cdot NH\cdot CO_2Me$, forms colourless crystals, m. p. 239—241° (decomp.), and when heated with slaked lime yields the diamine. It has not been found possible to diazotise the diamine and obtain the corresponding hydrocarbon; the product formed appears to be *methyl* iso*propylcarbazole*, $C_{16}H_{17}N$. It crystallises in glistening prisms, m. p. 124° (corr.), and yields a *picrate*, m. p. 166—167° (corr.).

3′-Methyl-4-*iso*propyldiphenamic acid,

$$NH_2\cdot CO\cdot C_6H_3Me\cdot C_6H_3Pr\cdot CO\cdot OH,$$

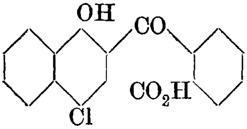
has m. p. 198—199°. J. J. S.

Preparation of *o*-4-Nitroso-1-hydroxynaphthoylbenzoic Acid. ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 223306).—*o*-4-*Nitroso*-1-*hydroxy*-β-*naphthoylbenzoic acid* (annexed formula) is prepared by treating finely-powdered *o*-1-hydroxy-β-naphthoylbenzoicacid with a concentrated solution of sodium nitrite, and keeping the paste well stirred at a temperature of 45° during six or eight hours, with further additions of water as necessary to keep it at a workable consistency. It forms sulphur-yellow crystals, m. p. 195° (the *sodium* salt is sparingly soluble), and on reduction yields *o*-4-amino-1-hydroxy-β-naphthoylbenzoic acid.



F. M. G. M.

Preparation of *o*-**4-Chloro-1-hydroxy-**β-**naphthoylbenzoic Acid.** ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 224538).—The action of ordinary chlorinating agents on *o*-1-hydroxy-β-naphthoylbenzoic acid is violent and leads to the formation of mixed products; it is now found that sulphuryl chloride in ethereal solution and at a low temperature gives a good yield of *4'-chloro-1'-hydroxy-β-naphthoyl-o-benzoic acid*,



bright yellow prisms, m. p. 211°. F. M. G. M.

Action of Light on Benzaldehyde in the Presence of Iodine. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 300—302. Compare this vol., i, 389, 561).—Among the products of this reaction, *iso*benzil, COPh·O·CPh:CPh·O·COPh, has now been identified. R. V. S.

Action of Light on *p*-**Tolualdehyde in the Presence of Iodine.** LUIGI MASCARELLI and G. RUSSI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 239—242. Compare this vol., i, 389, 561).—The results obtained were similar to those already recorded in the case of benzaldehyde. The aldehyde when exposed to light in the presence of iodine for three years yielded (1) *p*-toluic acid; (2) a *trimeric tolualdehyde*, forming thin, colourless, prismatic crystals, m. p. 215°; (3) p-*tolyl* p-*toluate*, a pale yellow oil, b. p. 213—217°/15 mm., identical with that prepared by the Schotten-Baumann reaction (b. p. 224—228°/20—21 mm.). R. V. S.

Nature of the Catalytic Action of Zinc Chloride by the Condensation of Aromatic Ketones with Amines. G. REDDELIEN (*Ber.*, 1910, **43**, 2476—2480. Compare this vol., i, 118). —Benzophenone condenses readily with aniline and its derivatives in presence of anhydrous zinc chloride, or of the corresponding zinc chloride amine salt, for example, aniline zinc chloride, $ZnCl_2(NH_2Ph)_2$. When the amine forms no additive compound with zinc chloride (for example, *m*-nitroaniline, *m*-aminophenol), no condensation takes place. The zinc chloride amine compounds are not hygroscopic, and they act only as amine carriers, whereas the elimination of water from compounds, $OH{\cdot}CR_2{\cdot}NHR$, is brought about by the high temperature of the reaction. There is no interaction when benzophenone and aniline zinc chloride alone are heated at 160°, reaction immediately beginning when aniline is introduced. Benzophenoneanil is partly decomposed by zinc chloride at 160° with the formation of the compound $ZnCl_2(NH_2Ph)_2$.

The additive compounds of zinc chloride with the toluidines, xylidine, and phenylenediamine also act as catalysts. Anhydrous zinc chloride also acts as a condensing agent when more is used at a higher temperature, and the reaction is continued for a longer period. It acts not as a catalyst, but in withdrawing water.

On heating acetophenone with aniline in presence of zinc chloride, the chief product is triphenylbenzene, m. p. 170°. When zinc chloride

aniline is used, acetophenoneanil is obtained as a pale yellow oil, b. p. 198—200°/37 mm., solidifying to colourless crystals, m. p. 41°. It dissolves in concentrated sulphuric acid with an intense yellow coloration.

The following keto-imines have been condensed by means of zinc chloride amine or zinc chloride:

*Bis-diphenylmethylene-*p*-phenylenediamine*, $CPh_2{:}N{\cdot}C_6H_4{\cdot}N{:}CPh_2$, crystallises in golden-yellow, jagged plates, m. p. 180°. p-*Phenylenediamine zinc chloride*, $ZnCl_2,NH_2{\cdot}C_6H_4{\cdot}NH_2$, forms bunches of colourless, microscopic needles.

Fluorenoneanil, $C(C_6H_4)_2{:}NPh$, separates in golden-yellow needles grouped in rosettes, m. p. 89°. *Fluorenone-*p*-toluidine* forms lustrous, golden-yellow needles, m. p. 124°.

*Diphenylenemethylene-*p*-aminophenol* forms large, lustrous, dark brown plates, which become yellow on heating, m. p. 218—219°.

*Bis-diphenylenemethylene-*p*-phenylenediamine* crystallises in lustrous, red needles, m. p 278°. E. F. A.

Keto-anils. MAX BUSCH and FERD. FALCO (*Ber.*, 1910, **43**, 2557—2564).—The easy production of keto-anils, NR:CR′R″, by the interaction of benzanilideimino-chloride and magnesium alkyl halogenides in ether (this vol., i, 729) led the authors to hope they had discovered a satisfactory method of testing the Hantzsch-Werner hypothesis of the stereoisomerism of tervalent nitrogen compounds (compare Straus and Ackermann, this vol., i, 241). *Deoxybenzoinanil*, $NPh{:}CPh{\cdot}CH_2Ph$, m. p. 89°, is ultimately obtained by the interaction of benzanilideimino-chloride and an excess of magnesium benzyl chloride; it forms slender needles and decomposes easily in alcoholic solution, especially by treatment with dilute sulphuric acid, into deoxybenzoin and aniline. When heated above 100° for two to three hours it is oxidised to a great extent to benzilanil; by exposing its solution in petroleum to sunlight for five to six hours, benzanilide and benzilanil are formed. (Equal molecular quantities of benzanilide-imino-chloride and magnesium benzyl chloride react in ether ultimately to form chiefly diphenylbenzenylamidine.)

Phenyl α-naphthyl ketoneanil, $NPh{:}CPh{\cdot}C_{10}H_7$, obtained from the product of the reaction between magnesium α-naphthyl bromide and benzanilideimino-chloride in ether, exists in two forms: long, monoclinic leaflets, m. p. 101°, and triclinic prisms, m. p. 95°. The former are obtained from concentrated, the latter from dilute, solutions, and either can be obtained from a solution of the other by inoculation. Despite the difference of m. p. and of crystalline form, the two substances are regarded as dimorphous forms of an individual substance and not as stereoisomerides, because they are identical as regards colour, solubility, and chemical behaviour (*hydrochloride*, m. p. 187—188°; *picrate*, m. p. 165°). C. S.

m-p-Ditolyl Ketone. JAMES LAVAUX and MAURICE LOMBARD (*Bull. Soc. chim.*, 1910, [iv], 7, 913—915).—The action of methylene chloride on toluene in presence of aluminium chloride leads to the production of a mixture of hydrocarbons, which on oxidation furnishes

m-p-ditolyl ketone as one product. The ketone and some of its derivatives are described.

The yield of hydrocarbons in the condensation is about 60% of the theoretical, and the product consists of ditolylmethane and dimethylanthracene in the proportion 20 : 1. The ditolylmethane boils at 288—290°, and on oxidation with chromic acid in acetic acid furnishes *benzophenone*-3 : 4′-*dicarboxylic acid*, m. p. 337° (corr.), which crystallises from alcohol in small needles, and m-p-*ditolyl ketone*, m. p. 70·5°, which forms acicular crystals from boiling alcohol, and is readily soluble in organic solvents, particularly in chloroform; the *oxime*, m. p. 128—129°, forms needles, and the *semicarbazone*, m. p. 183° (approx.), crystallises from alcohol.

The constitution of the ketone is established by the fact that it yields on fusion with potassium hydroxide, *m*- and *p*-toluic acids, and the amides of these two acids on treatment with sodamide. T. A. H.

Reaction between *p*-Benzoquinone and Hydrogen Chloride. Arthur Michael and Philip H. Cobb (*J. pr. Chem.*, 1910, [ii], **82**, 297—306).—The author takes exception to Thiele's and to Posner's explanation of the action of hydrogen chloride or bromide on *p*-benzoquinone by the theory of partial valency; this theory requires that halogenated quinols should be the first products of the reaction, whereas the author shows that in chloroform or carbon tetrachloride the initial product is quinhydrone or a mixture of quinhydrone and chloroquinone. C. S.

Mechanism of Quinone Reactions. Reply to Posner. Arthur Michael (*J. pr. Chem.*, 1910, [ii], **82**, 306—321).—The author gives a further reply to Posner's criticisms (Abstr., 1904, i, 1029; 1909, i, 809) of his explanations of the reactions between *p*-benzoquinone and hydrogen chloride, aniline, and thiophenol (Abstr., 1904, ii, 164; 1909, i, 494). C. S.

Quinonoid Compounds. XXIII. Oxidation of Aniline. Richard Willstätter and Rikō Majima (*Ber.*, 1910, **43**, 2588—2593). —A new example of ortho-condensation during the oxidation of aniline is furnished by the use of ferric chloride. A solution of aniline in 6% sulphuric acid is treated at 30° with a concentrated solution of ferric chloride (equiv. to $2\frac{1}{2}O$), whereby a mixture of aniline-black and dianilinobenzoquinone is produced, from which the latter may be isolated by sublimation in a vacuum, by extraction with boiling chloroform, or by extraction with nitrobenzene and sublimation at 15 mm. in carbon dioxide of the brown, crystalline product obtained from the cold solution. By reduction with tin and warm hydrochloric acid, dianilinobenzoquinone is converted into anilinoquinol, a solution of which in *N*-hydrochloric acid is oxidised by careful treatment with *N*/10-ferric chloride to *anilino*-p-*benzoquinone*,

$$O:C<\begin{matrix}C(NHPh):CH\\CH=\!=\!=CH\end{matrix}>C:O,$$

m. p. 117—118°. This substance, which is much more intensely coloured than more complex anilinobenzoquinones, forms glistening,

bronze plates, which are brownish-yellow by transmitted light, gives intensely red solutions, is stable to sulphurous acid, and is reduced by zinc and acetic acid to dihydroxydiphenylamine.

An aqueous 2% solution of aniline is oxidised by Caro's method with saturated potassium persulphate in the presence of calcium carbonate; the red, crystalline product, m. p. 252°, which is regarded as *dianilino-p-benzoquinoneimine*, $NH:C<\begin{matrix}C(NHPh):CH\\CH:C(NHPh)\end{matrix}>C:O$, yields dianilinobenzoquinoneanil with aniline and acetic acid, is very stable to lead dioxide and sulphuric acid, and dissolves in concentrated sulphuric acid with a brownish-violet colour, which turns violet by the addition of alcohol and warming. C. S.

Action of *p*-Benzoquinone on Diamines and Esters of Amino-acids. WILHELM SIEGMUND (*J. pr. Chem.*, 1910, [ii], **82**, 409—414. Compare Schlenk, Abstr., 1909, i, 807; Fischer and Schrader, this vol., i, 270).—By cooling a hot solution of *p*-benzoquinone (2 mols.) and diaminodiphenylmethane (1 mol.) in a little benzene, glistening, black, rhombic plates of a *substance*, $C_6H_4O_2,CH_2(C_6H_4\cdot NH_2)_2$, m. p. 72—73°, are obtained, which gives a violet coloration with concentrated sulphuric acid. In a similar way, *p*-benzoquinone and diaminostilbene yield brownish-black, metallic crystals of a *substance*,

$$3C_6H_4O_2,2C_2H_2(C_6N_4\cdot NH_2)_2,$$

m. p. 130°, which gives a yellow coloration with sulphuric acid. A benzene solution of *p*-benzoquinone and methyl *p*-aminobenzoate in the proportion 3 : 2 yields, after the addition of petroleum, dark red leaflets of the *substance*, $C_6H_4O_2,2NH_2\cdot C_6H_4\cdot CO_2Me$, m. p. 83°, which by prolonged boiling with *p*-benzoquinone in alcohol is converted into *methyl p-benzoquinone-2 : 5-diaminobenzoate*,

$$CO_2Me\cdot C_6H_4\cdot NH\cdot C<\begin{matrix}CO\cdot CH\\CH\cdot CO\end{matrix}>C\cdot NH\cdot C_6H_4\cdot CO_2Me,$$

which crystallises in brown needles, and decomposes when heated. C. S.

Stable Primary Nitrosoamine. GUSTAV HELLER and APOSTOLOS SOURLIS (*Ber.*, 1910, **43**, 2581—2588).—4 : 6-Dinitroresorcinol (which forms a *diacetate*, m. p. 139°, and a *dibenzoate*, m. p. 343—344°) is suspended in glacial acetic acid and reduced by stannous chloride and 23% hydrochloric acid below 60°; by the addition of sodium acetate and acetic anhydride, the product of reduction is isolated as *6-nitro-4-acetylaminoresorcinol*, m. p. 261° (decomp.), which is hydrolysed by concentrated hydrochloric acid, yielding the *hydrochloride*, m. p. above 300°, of *6-nitro-4-aminoresorcinol*, m. p. 160—161° (decomp.). The reduction of 4 : 6-dinitroresorcinol by tin and hydrochloric acid and the treatment of the product with acetic anhydride yield *4 : 6-diacetylaminoresorcinol*, m. p. 335° (decomp.), which forms a *dibenzoate*, m. p. 214°.

6-Nitro-4-nitrosoamino-3-hydroxy-o-benzoquinoneoxime,

$$O:C<\begin{matrix}C(:NOH)\cdot C(OH)\\C(NO_2)=\!=\!=CH\end{matrix}>C\cdot NH\cdot NO,$$

obtained from aqueous 6-nitro-4-aminoresorcinol hydrochloride or

hydrobromide and sodium nitrite (2 mols.) at 0°, forms dark yellow, hexagonal plates, and explodes when heated. The substance is regarded as a nitrosoamine, and not as an *anti*-diazohydroxide, because it does not react with acetyl chloride or acetic anhydride, and its solution in alcoholic hydrogen chloride does not combine directly with alkaline β-naphthol; its solution in concentrated hydrochloric acid is very stable, and the diazonium salt thereby produced combines at once with alkaline β-naphthol, forming *6-nitro-3-hydroxy-1 : 2-quinoneoxime-4-azo-β-naphthol.* The substance shows the character of a quinone-oxime, a 1% solution in dilute acetone dyeing chromed wool a tobacco-brown colour; in faintly alkaline β-naphthol solution, the dyed wool acquires a distinct blue tinge. When the nitrosoamine in concentrated hydrochloric acid is treated with copper powder in the cold, the *hydrochloride*, $C_6H_3O_5N_2Cl,HCl$, m. p. 204—205°, of *4-chloro-6-nitro-3-hydroxy-1 : 2-quinoneoxime*, yellow needles, m. p. 155°, is obtained, a 1% solution of which produces a clearer and yellower tone on chromed wool than the nitrosoamine. C. S.

Preparation of Acetylchloroaminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 224073).—Acetylchloroaminoanthraquinones, analogous to the phenyl compounds described by Bender (Abstr., 1887, 44), are readily obtained by the action of hypochlorous acid on an aqueous or dilute acetic acid solution or suspension of the required acetylaminoanthraquinone; if glacial acetic acid is employed, nuclear substituted derivatives are formed.

Acetylchloro-β-aminoanthraquinone is prepared by heating the components together on the water-bath until a permanent yellow colour is obtained; it forms small needles, somewhat soluble in nitrobenzene.

Acetylchloro-α-aminoanthraquinone requires greater excess of hypochlorous acid and more prolonged heating for its preparation.

These compounds are initial substances in the preparation of dyes.

F. M. G. M.

Preparation of β-Anthraquinonylcarbimide from β-Aminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 224490).—*β-Anthraquinonylcarbimide*, m. p. 173°, is prepared by treating β-aminoanthraquinone with carbonyl chloride in nitrobenzene or xylene solution and keeping the mixture at the ordinary temperature until no red coloration is produced with dilute alcohol. The liquid is then heated to a temperature of 130—150°, when, on cooling, the product separates in colourless crystals. By treatment with moderately concentrated sulphuric acid, it is decomposed, yielding β-aminoanthraquinone with evolution of carbon dioxide.

F. M. G. M.

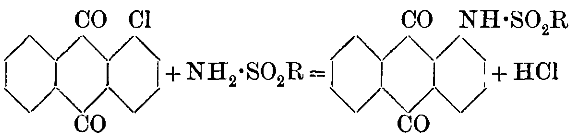
[Preparation of Aminoanthraquinone Thio-ethers.] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224589).—An account of the preparation of dyes obtained by the action of aliphatic mercaptans on negatively substituted anthraquinone derivatives (containing either halogen, nitro- or sulphonic groups) in aqueous

alkaline solution. The following compounds are mentioned: 1-*Amino-4-ethylthiolanthraquinone,* bronze prisms; 1-*benzoylamino-4-ethylthiolanthraquinone,* bronze needles; 1-*acetylamino-4-ethylthiolanthraquinone,* red crystals; 1-*amino-2:4-diethylthiolanthraquinone,* red leaflets: 1:5-*diamino-4:8-diethylthiolanthraquinone,* steel-blue leaflets; *sodium 1-ethylthiolanthraquinone-5-sulphonate,* orange leaflets; 1:5-*diethylthiolanthraquinone,* yellow leaflets; *sodium* 1:4-*diethylthiolanthraquinone-8-sulphonate,* red needles.

The colour of the solutions of these subtances in various solvents is tabulated in the patent. F. M. G. M.

[Preparation of Benzoylaminoanthraquinones.] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 225232).—A tabulated list of substituted benzoylamino- and dibenzoyldiamino-anthraquinones and their condensation products, with the colours of their solutions in pyridine, concentrated sulphuric acid, when dyed on wool, and in the vat. F. M. G. M.

Preparation of Arylsulphonaminoanthraquinones. FRITZ ULLMANN (D.R.-P. 224982).—When substituted halogen anthraquinones are heated with arylsulphonamides and potassium carbonate in the presence of copper acetate in boiling nitrobenzene solution (or, if necessary, at higher temperatures), the following reaction takes place:



1-p-*Toluenesulphonaminoanthraquinone,* long, yellow needles, m. p. 225°, was obtained from 1-chloroanthraquinone and *p*-toluenesulphonamide.

2-*Iodoanthraquinone,* needles, m. p. 170°, is prepared by the method described for 1-iodo-2-methylanthraquinone (Scholl, Abstr., 1907, i, 540), and when treated as above yielded 2-p-*toluenesulphonaminoanthraquinone*; this forms yellow needles.

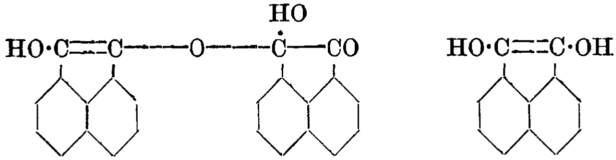
1:2-*Anthraquinonylsulphonaminoanthraquinone,* prepared from 1-chloroanthraquinone and *anthraquinone-2-sulphonamide,* is insoluble in the ordinary organic solvents, but dissolves in concentrated sulphuric acid, yielding a red solution.

1:5-*Dibenzenesulphonyldiaminoanthraquinone,* a yellow, crystalline powder, was obtained from 1:5-dichloroanthraquinone and benzenesulphonamide. F. M. G. M.

Preparation of Reduction Products of Acenaphthenequinones. KALLE & Co. (D.R.-P. 224979).—Reduction products from acenaphthenequinones have previously been studied; it is found that less energetic reduction, or the employment of milder reducing agents, gives rise to different products.

The *compound* (probably I) is produced by the action of alkaline

reducing agents; it forms yellow prisms, m. p. 248°, may be crystallised from tetrachloroethane, and yields a *hydrogen sulphite* and an *acetyl*



(I.) (II.)

derivative on treatment respectively with sodium hydrogen sulphite or acetic acid. The second *compound* (probably II) is obtained with acid, neutral, or alkaline reducing agents; it crystallises from alcohol in needles, has m. p. 254°, and forms two series of salts which are soluble in water. One alkali salt is pale blue, the other (when excess of alkali is employed) a deep violet blue; the *magnesium* salts are colourless. This substance can be acetylated, and combines with sodium hydrogen sulphite and with hydroxythionaphthens to form vat dyes.

F. M. G. M.

Preparation of Anthraquinone Derivatives. KINZLBERGER & Co. (D.R.-P. 223210).—When anthraquinone is heated at 160° with sodium hydroxide and zinc dust (or other alkaline reducing agents) it yields a *dianthranol*, $C_{28}H_{18}O_2$, m. p. 230°. This on oxidation with alkaline potassium permanganate gives a *compound*, $C_{28}H_{16}O_2 = CO<{C_6H_4 \atop C_6H_4}>C:C<{C_6H_4 \atop C_6H_4}>CO$, forming yellow crystals, which turn green on pressure and blacken at 300° without fusion.

F. M. G. M.

Behaviour of Some Derivatives of Phenylhydroxylamine. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 122—129).—Additional reasons are adduced for the formula assigned (this vol., i, 552) to the product of the action of nitrosobenzene on safrole, which is identical with that obtained by the action of phenylhydroxylamine on methylenedioxycinnamaldehyde. The double linking between carbon atoms appears to be connected with the fact that the substance is coloured, since the analogous derivatives of benzaldehyde and phenylacetaldehyde are white. Moreover, *β-cyclo*citral yields a colourless derivative, so that the double linking in the above compound is probably in the side-chain. Benzoylacetaldehyde also yields a yellow derivative, although the constitution of the latter is not quite clear.

The *N*-phenyloximes described yield with hydroxylamine the corresponding oxime and phenylhydroxylamine, and they are rapidly affected by light. The action of light has been investigated further in the case of some analogous compounds. The cinnamaldehyde derivative, when exposed to light in sealed tubes freed from air, yields cinnamaldehyde and cinnamylideneaniline, CHPh:CH·CH:NPh. At the same time small quantities of other substances are formed, and an odour of *iso*nitrile is perceptible. The benzaldehyde derivative, when

exposed to sunlight and air, forms benzaldehyde, nitrosobenzene, and benzanilide (compare Ciamician and Silber, Abstr., 1905, i, 335), in addition to small quantities of azoxybenzene, *o*-hydroxyazobenzene, and dibenzaniline. Nitrosophenylhydroxylamine, O:NPh:N·OH, should form diazobenzene hydroxide analogously, and, in fact, an alkaline solution of it containing α-naphthol deposits benzeneazonaphthol when exposed to light. The process is rapid enough to have application in photography. The salts of the isomeric phenylnitroamines,

NPh:NO·OH,

are acted on similarly, but more slowly. The sodium derivative of nitrosophenylhydroxylamine yields nitrosobenzene rapidly in the light. Unsaturated nitro-derivatives, such as 7-nitrostilbene and piperonalnitroethane, are also decomposed by light.

When β-*cyclo*citral and phenylhydroxylamine are kept in a sealed tube in the dark for some days, N-*phenyl*-β-cyclo*citraloxime*, $C_{16}H_{21}ON$, is formed. It forms long, colourless needles, m. p. 109—110°. It is acted on by permanganate, nitrosobenzene being formed, and it is rapidly hydrolysed by dilute sulphuric acid. When it is exposed to light, it quickly resinifies, an odour of *cyclo*citral and *iso*nitrile is observed, and nitrosobenzene is formed. The last-named substance can be recognised by means of test-papers impregnated with hydroxylamine hydrochloride, sodium carbonate, and α-naphthol. β-cyclo*Citraloxime*, $C_{10}H_{17}ON$, prepared by the action of hydroxylamine on the above ether, or on β-*cyclo*citral, forms large, colourless rhomboidal crystals, m. p. 84°, has a characteristic odour, is volatile in steam, and is readily hydrolysed by acids. β-cyclo*Citralsemicarbazone*, $C_{11}H_{19}ON_3$, forms a felted mass of colourless needles, m. p. 209° (decomp.); Tiemann (Abstr., 1901, i, 158, 599) describes a semicarbazone, m. p. 166—167°. By the action of phenylhydroxylamine on benzoylacetaldehyde, a *substance*, $C_{15}H_{13}O_2N$, is obtained, crystallising in orange needles, m. p. 158° (decomp.), which when warmed with permanganate yields nitrosobenzene, but is stable towards light. R. V. S.

Nerol and Thymol in French Lavender Oil. F. ELZE (*Chem. Zeit.*, 1910, **34**, 1029).—From a French lavender oil, having D^{15} 0·889, a_D −6°20′, and saponification number 99, a portion boiling at 85—100°/5 mm. was separated by distillation under reduced pressure. From this thymol was obtained by extraction with a dilute solution of sodium hydroxide, and from the residue nerol was isolated as the acid phthalate. T. A. H.

Molecular Rearrangements in the Camphor Series. III. Oxidation Products of *l*- and *d*-Laurolene. WILLIAM A. NOYES and C. G. DERICK (*J. Amer. Chem. Soc.*, 1910, **32**, 1061—1064. Compare Abstr., 1909, i, 133, 560).—Contrary to the authors' previous statements, the diketone obtained by oxidising *l*-laurolene does not undergo condensation readily. It has b. p. 204°/750 mm. (corr.); the optical activity varies with the method of preparation. The *disemicarbazone* has m. p. 194° (corr.), but the *dioxime* and *phenylhydrazone* are oily.

The rotation of *d*-laurolene varies with the method of preparation; a specimen prepared by the action of sodium nitrite on the hydro-

chloride of aminolauronic acid had $[\alpha]_D^{26\cdot2}$ 28·15°, whilst the density and b. p. were identical with that of the *l*-form. Oxidation with cold alkaline permanganate gave a *diketone*, $C_8H_{14}O_2$; the *disemicarbazone*, after melting at 192° (corr.), solidified, and then had m. p. 225° (corr.).

The properties of the oxidation products of laurolene are in accord with Eykman's representation of the structure of this substance (Abstr., 1907, i, 378). W. O. W.

Molecular Rearrangements in the Camphor Series. IV. Synthesis of Laurolene. WILLIAM A. NOYES and L. P. KYRIAKIDES (*J. Amer. Chem. Soc.*, 1910, **32**, 1064—1068. Compare preceding abstract).—The dimethyl*cyclo*pentanone obtained by heating *d*-$\alpha\delta$-dimethyladipic acid with lime is optically inactive. Grignard'sreaction was applied to convert the product into 1 : 2 : 3-*trimethyl*cyclo*pentanol*, $C_8H_{16}O$, a liquid having b. p. 56—60°/8 mm., D_4^{15} 0·9121, $n^{16\cdot7}$ 1·4554. This substance loses water when heated, and is converted into laurolene; the transformation, however, is more easily effected by Zelinsky's method (Abstr., 1902, i, 2). The hydrocarbon thus prepared has b. p. 120—122°, $n^{16\cdot5}$ 1·4461, and on oxidation furnishes a diketone identical with that obtained from aminolauronic acid. The refractive index of synthetic laurolene is slightly less than that of the natural product, possibly through the presence of some ψ-laurolene.

The structure of laurolene as Δ^1-1 : 2 : 3-trimethyl*cyclo*pentene is, therefore, fully established. W. O. W.

Molecular Rearrangements in the Camphor Series. V. Mechanism of the Reactions by which Laurolene is Formed. WILLIAM A. NOYES (*J. Amer. Chem. Soc*, 1910, **32**, 1068—1070. Compare preceding abstracts).—A theoretical discussion. A methyl group is assumed to become detached and to unite with an adjacent carbon atom in the formation of laurolene from camphanic acid (Crossley and Renouf, Trans., 1906, **89**, 27) and from aminolauronic acid or anhydride. W. O. W.

Some Thujene Derivatives. IWAN L. KONDAKOFF and W. SKWORZOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 497—504. Compare Abstr., 1904, i, 438).—The authors consider that the structure of the compounds in the thujene series has not yet been satisfactorily settled. Thujene has never yet been obtained in a pure state, the product consisting of a mixture of dicyclic thujenes together with terpene and some other hydrocarbon. When the thujene obtained by the xanthate method is treated several times with 1% potassium permanganate, a tricyclic hydrocarbon or some stereoisomeric thujene was obtained, having b. p. 147·5—149·5°, D^{16} 0·8220, n_D 1·44809, $[\alpha]_D$ +109·09°.

By removing hydrogen bromide from thujyl bromide, an unsaturated *alcohol* was obtained, b. p. 218—221°/760 mm., 96—100°/10 mm., D^{20} 0·9174, n_D 1·47936, $[\alpha]_D$ +13·22°. Similarly, from the chloride, the *alcohol* obtained has b. p. 205—208°, D_4^{17} 0·8947, n_D 1·46128, $[\alpha]_D$ +23·22°. The taste and odour of both alcohols are alike, and similar to that of menthol and terpeneol. They do not yield urethanes, are largely converted into resins by the action of hydrochloric acid and

of succinic anhydride at 150°, are readily oxidised by concentrated potassium permanganate, and readily lose water. They are probably tertiary alcohols containing a five-membered ring, and are very similar to the alcohol obtained by Semmler from sabinene (Abstr., 1907, i, 145), excepting that in the latter the double bond is in the side-chain, whereas in the former it occurs in the ring.

By the action of hydrochloric acid on *iso*thujene, and also on the alcohol described above, a *dihydrochloride*, $C_{10}H_{18}Cl_2$, b. p. 121·5—125·5°/16 mm., D^{20} 1·0697, n_D 1·48458, $[\alpha]_D$ +1·86°, is obtained, together with resinised products. When treated with sodium acetate, a *hydrocarbon*, $C_{10}H_{16}$, b. p. 176—180°, D^{18} 0·8540, n_D 1·47586, $[\alpha]_D$ +3·11°, was obtained, the constitution of which may be (II) or (III) if formula (I) is taken as that of *iso*thujene.

$$CHMe_2\cdot CH<\begin{array}{l}CMe:CMe\\ CH{=}CH\end{array} \qquad CHMe_2\cdot C\leqslant\begin{array}{l}CHMe\cdot CMe\\ CH{-\!-}CH\end{array}$$

(I.) (II.)

$$CHMe_2\cdot C\leqslant\begin{array}{l}CMe:CMe\\ CH{-\!-}CH_2\end{array}.$$

(III.)

Z. K.

Essential Oils. ROURE-BERTRAND FILS (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1910, [iii], 1, 34—62).—[JUSTIN DUPONT and LOUIS LABAUNE.]—It has been shown previously that when cinnamyl alcohol in toluene is treated with hydrogen chloride at 100°, a chloride, C_9H_9Cl, is formed (this vol., i, 185). This is now shown to be cinnamyl chloride. On treatment with silver nitrate in alcohol, it yields a mixture of products, from which, by the action of sodium and subsequent fractional distillation, α-phenylallyl ethyl ether and cinnamyl ethyl ether were isolated. In addition, the mixture contains α-phenylallyl alcohol and cinnamyl alcohol (compare Charon, *Bull. Soc. chim.*, 1910, [iv], 7, 86). A good yield of the supposed linalyl chloride described already may be obtained by treating either linalool or geraniol in dry benzene with phosphorus trichloride (this vol., i, 184).

Hydrogen bromide reacts with geraniol or with *l*- or *d*-linalool, dissolved in toluene and maintained at 100°, to form a *bromide*, D^{15} 1·1450, α_D ±0, n_D^{15} 1·507, b. p. 102—103°/6 mm., and this, when heated with potassium acetate in presence of toluene, yields linalyl acetate. When the bromide is treated with sodium ethoxide, it yields geranyl ethyl ether, b. p. 218°; with silver hydroxide, it gives linalool, and with silver nitrate, it furnishes linalool, geranyl ethyl ether, and possibly linalyl ethyl ether. In view of this complex reaction with silver nitrate, it is difficult to assign a constitutional formula to the bromide or the corresponding chloride.

Orange flowers collected in May and in October, 1909, yielded, by extraction with light petroleum, 736·3 and 663·6 grams respectively of total essential oil per 1000 kilos. of flowers. The May oil had D^{15} 0 8899, n_D^{15} 1·478, $\alpha_D = -0°48'$, acid value 0·7, saponification value 70·2, esters 24·6%, alcohols 51·0%, methyl anthranilate 3·53%. The

autumn oil had D^{15} 0·8887, n_D^{15} 1·476, $\alpha_D = -4°6'$, acid value 1·0, saponification value 95·8, esters 33·4%, alcohols 57·0%, methyl anthranilate 2·74%. These extracted oils differ from oil of neroli (distilled oil) in being lævorotatory, indicating that a change in rotation occurs as the result of distillation in steam. The higher yield of oil in May and the greater richness of this oil in methyl anthranilate is probably due to more active metabolism in the plant at that period and to the warmer temperature. Extracted orange flower oil usually contains over 7·0% of methyl anthranilate, and the low yield in these two samples may have been a result of the severe winter preceding the orange flower harvest of 1909. Analyses of the two oils, after removal of methyl anthranilate by Hesse and Zeitschel's process (Abstr., 1901, ii, 209), gave constants indicating that the May oil was poorer in combined and total alcohols than the October oil, the quantity of free alcohols being about the same; similarly, the October oil was richer in the primary alcohols, geraniol and nerol. It seems likely, therefore, that in May the flowers draw their supply of oil from the young branches, and in October from the older branches. The results also afford a further proof of the formation of terpene compounds in green organs.

Myrica Gale yielded, by steam distillation, 0·0443% of a greenish-yellow, volatile oil, having D^{25} 0·8984, α_D^{20} $-5°16'$, acid value 3·48, saponification value 17·98, esters 5·1%, total alcohols 14·4%, and free alcohols 10·5%. The oil exhibited a powerful purgative action, as did also a resin contained in the plant.

Java patchouli leaves furnished 0·803% of oil having D^{15} 0·9564, $\alpha_D = -28°8'$, saponification value 6·3, saponification value of acetylated oil 40·4.

Oil of *Mentha arvensis* var. *Javanica* had D^{15} 0·9979, $\alpha_D = +0°24'$, acid value 69·8, saponification value 49·7, saponification value after acetylation 153·3, corresponding with esters 17·5%, total menthol 48·2%, free menthol 34·4%, ketones or aldehydes, traces or none. The oil did not deposit crystals at $-15°$.

Ylang-ylang oil from Mayotte had D^{15} 0·9324, $\alpha_D = -47°40'$, acid value 1·0, saponification value 113·4, corresponding with esters 39·7%, total alcohols 41·0%, and free alcohols 9·8%.

An oil from French Guiana had D^{15} 0·8864, α_D $-0°2'$, total alcohols 71·3%, esters 5·8%, and dissolved to the extent of 80% in sodium hydrogen sulphite solution. The oil had a lemon-like odour, and was described as derived from *Andropogon Nardus*, L. The results indicated that it was derived from *A. citratus*, De Cand., and was abnormally rich in citronellal and geraniol.

In continuation of previous work (this vol., i, 401), Delépine finds that samphire oil contains dipentene, not limonene; in addition to the constituents already described, the oil contains traces of two phenols (one crystalline, and the other possessing an odour of cresote), and a small quantity of an alcohol having an odour of roses, with other indefinite products. T. A. H.

Essential Oils. SCHIMMEL & Co. (*Bericht*, October, 1910).—The fruits of *Pimenta acris* from Mauritius yielded 3·3% of bright brown

oil, D^{15} 0·9893, α_D $-1°20'$, n_D^{20} 1·51902, eugenol 70% (compare *Bull. Imp. Inst.*, 1910, **8**, 4).

Camphor oil from German East Africa had D^{15} 0·9203, α_D $+39°42'$, n_D^{20} 1·47753, and deposited camphor on cooling.

Cocking (*Chemist and Druggist*, 1910, **77**, 19) has devised a method for detecting "Illurin balsam" in copaiba balsam, depending on the fact that if oil be distilled from these balsams in ten equal fractions, those from copaiba balsam show increasing laevorotation, whilst those from Illurin balsam show increasing dextrorotation.

Bergamot oil adulterated with ethyl citrate yields on evaporation to constant weight on the water-bath, a residue having a saponification value above that found for a similar residue from genuine oil, namely, 160, and the increase in the value may be used to obtain a rough indication of the extent of the adulteration. In the saponified product citric acid may be detected by means of calcium chloride or by Deniges' test (Abstr., 1899, ii, 454), the acid being first converted into acetonedicarboxylic acid by means of lead dioxide. Genuine bergamot oil contains only traces of citric acid, which, however, can be detected by Denigès' reaction. Genuine bergamot oil shows the same saponification value after heating at 100° during thirty or sixty minutes with *N*/2-potassium hydroxide in alcohol, but if terpinyl acetate is present the saponification value increases with longer heating, and in any case is higher than that shown by genuine oil. Glyceryl acetate may be detected by Jeancard and Satie's method, which depends on the partial extraction of the glyceryl acetate with water. For the detection and estimation of sophistication by esters of non-volatile acids, 1·5 to 2 grams of oil is treated in the ordinary way for the determination of the total saponification value [acid and ester values]. The saponified product is made distinctly alkaline, evaporated to dryness, the residue acidified with sulphuric acid, and the acid value of the distillate determined. The difference between the "total saponification value" and the "volatile acid value" for genuine oil is not more than 7. These methods are applicable also to lavender and "petit grain" oils.

In Rèunion geranium oil, linalool, α-terpineol, and phenylethyl alcohol were found in addition to traces of menthol and of an alcohol with an odour recalling that of borneol. Terpinenol may also be present.

Garlic contains according to Rindqvist (*Apoth. Zeit.*, 1910, **25**, 105) a glucoside, *alliin*, which is decomposed by a specific enzyme, *allisin*, yielding garlic oil and lævulose.

A Chinese peppermint oil had D^{15} 0·9187, α_D $-44°2'$, ester value 43·9, total menthol 64·0%, and was soluble in 2·5 or more volumes of 70% alcohol.

Japanese peppermint oil contains Δ^1-menthenone, b. p. 235—237°/752 mm., D^{15} 0·9382, D^{20} 0·9343, α_D $+1°30'$, n_D^{20} 1·48411 (compare Wallach, Abstr., 1908, i, 812). The semicarbazone exists in the sparingly soluble α-form already described by Wallach (*loc. cit.*), and also in a readily soluble *β-form*, m. p. 171—172°. With hydroxylamine it forms an *oxime*, m. p. 107—109°, and an *oxamino-oxime*, m. p. 164—165°, which closely resembles the corresponding derivative of

carvenone, and must be constituted in an analogous manner, thus: $NH\cdot OH\cdot CMe<\begin{matrix}CH_2\cdot C(NOH)\\CH_2 \text{------} CH_2\end{matrix}>CHPr^{\beta}$. The ketone forms an unstable *dibromide*. With dehydrating agents, it yields *p*-cymene, and is oxidised by ferric chloride to thymol. Phosphorus pentachloride converts it into monochloroterpinene, and this on reduction with sodium in alcohol yields α-terpinene. On oxidation with permanganate the ketone furnishes formic acid, *α-hydroxy-α-methyl-δ'-*iso*propyladipic acid*, m. p. 143°, *α-*iso*propyl-γ-acetylbutyric acid* (the *semicarbazone* has m. p. 158—159°), and α-*iso*propylglutaric acid, the third acid resulting from further oxidation of the second, and the fourth in like manner from the third. These reactions can best be explained by the formula assigned to the ketone by Wallach (*loc. cit.*). For the characterisation of the ketone in essential oils, it is best isolated as the compound with sodium hydrogen sulphite, and identified by means of the α-semicarbazone. According to Murayama, Japanese peppermint oil also contains *l*-limonene (*J. Pharm. Chim.*, 1910, [vii], 1, 549).

A sage oil from Cyprus had D^{15} 0·9263, α_D $-6°15'$, n_D^{20} 1·46664, acid value 0, ester value 6·4, and acetyl ester value 36·0, and resembles Corfu sage oil.

From the first runnings of the distillation of sandalwood, the following constituents not previously observed have been isolated: (1)-Santenone, $C_9H_{14}O$, m. p. 58—61°, b. p. 193—195°, α_D $-4°40'$ in alcohol, is identical with the ketone prepared by Aschan (Abstr., 1908, i, 94) and by Semmler, and named by the latter π-norcamphor (Abstr., 1907, i, 1062); it yields a liquid *oxime*, b. p. 110—113°/6 mm., from which the ketone is not regenerated by warming with acids. (2) "Santenone alcohol," $C_9H_{16}O$, m. p. 58—62°, b. p. 196—198°, is apparently identical with Semmler's π-nor*iso*borneol (*loc. cit.*); on oxidation it yields santenone (π-norcamphor), furnishes a liquid *phenylurethane*, and is not etherified when warmed with alcohol and sulphuric acid. The isomeric alcohol (Aschan's santenol, *loc. cit.*; Semmler's π-norborneol, *loc. cit.*) on the contrary is etherified under these conditions, and yields, for example, *santenyl methyl ether*, $C_{10}H_{18}O$, b. p. 177—179°, D^{15} 0·9251, n_D^{20} 1·45841. It is suggested that Semmler's π-norborneol (Aschan's santenol) should now be called *iso*santenol and his π-nor*iso*borneol should be named santenol. (3) A *hydrocarbon*, $C_{11}H_{18}$, b. p. 183°, D^{15} 0·9133, D^{20} 0·9092, α_D $-23°55'$, n_D^{20} 1·47860, which may prove to be identical with Semmler's nor*tricyclo*eksantalane (Abstr., 1907, i, 432), since the latter, in view of Semmler's more recent work, must have the formula $C_{11}H_{18}$. (4) Nor*tricyclo*eksantalal, $C_{11}H_{16}O$, b. p. 86—87°/6 mm., 222—224°/761 mm., D^{20} 0·9938, α_D $-38°48'$, n_D^{20} 1·48393, is identical with Semmler's product (this vol., i, 573). It yields a liquid *oxime*, b. p. 135—137°/7 mm., and on oxidation by air in dilute alkali furnishes the corresponding *acid*, m. p. 91—93°, α_D $-33°17'$ (in alcohol). On oxidation with permanganate, teresantalic acid is formed. The aldehyde can also be obtained from normal sandalwood oil. (5) Teresantalol, $C_{10}H_{16}O$, m. p. 112—114°, identical with Semmler and Bartlett's product (Abstr., 1907, i, 703) prepared from teresantalic acid. (6) *iso*Valeraldehyde.

Müller's santalone (Abstr., 1900, i, 678) was isolated by means of the semicarbazone. It occurs associated with an isomeric *ketone*, yielding a *semicarbazone*, m. p. 208—209°, and an *oxime*, m. p. 100° (approx.). The sesquiterpene portion of the oil was separated by fractional distillation into α-santalene, b. p. 118°/7 mm., 252°/753 mm., D^{15} 0·9132, α_D −3°34′, n_D^{15} 1·49205, and β-santalene, b. p. 125—126°/7 mm., D^{20} 0·8940, α_D −41°3′, n_D^{20} 1·49460 (compare Semmler, Abstr., 1907, i, 781). It is probable that pure α-santalene is slightly dextrorotatory. On hydration, α-santalene furnishes a tertiary alcohol, $C_{15}H_{26}O$, b. p. 154—157°/5—6 mm., D^{15} 0·9787, D^{20} 0·9753, n_D^{20} 1·51725, which has a cedar-like odour, and on treatment with formic acid loses water. The portion of the hydrocarbon recovered from the hydration process is different from the original material (compare von Soden and Müller, Abstr., 1899, i, 924).

Brassica juncea seed from India yielded an oil having D^{15} 0·9950, α_D +0°12′, n_D^{20} 1·51849, and soluble in 10 vols. of 70% alcohol. It boiled for the most part between 150—160° and 174—178°. The principal constituents were dimethyl sulphide, allyl cyanide, allylthiocarbimide (40%), and a *crotonylthiocarbamide* (50%), b. p. 175—176°, D^{15} 0·994, α_D +0°3′, n_D^{20} 1·52398, which furnished a *thiocarbamide*, m. p. 69—70°.

Juniper berry oil contains camphene (compare Abstr., 1909, i, 818).

Chamaecyparis Lawsoniana furnished 1% of citron-yellow oil, D^{15} 0·9308, α_D +23°48′, n_D^{20} 1·48844, acid value 3·7, ester value 61·6, acetyl ester value 78·8, containing some decaldehyde (?).

The leaves of *Cinnamomum glanduliferum* contained *d*-camphor.

Dacrydium Franklinii wood yielded an oil, D^{15} 1·0443, α_D +0°6′, n_D^{20} 1·53287, containing much methyleugenol with some eugenol.

Eugenia apiculata leaves furnished 1·27% of brown oil, D^{15} 0·892, α_D +12°40′, n_D^{20} 1·47821, acid value 5·5, ester value 25·8, and acetyl ester value 65·3.

Perilla nankinensis leaf oil, D^{15} 0·9265, α_D −90°, n_D^{20} 1·49835, contains an *aldehyde*, b. p. 91°/4·5 mm., 104°/9 mm., 235—237°/750 mm., D^{20} 0·9645, D^{15} 0·9685, $[\alpha]_D$ −150·7°, n_D^{20} 1·50693, which yields an *oxime*, m. p. 102°, and a *phenylhydrazone*, m. p. 107·5°. The corresponding *acid* has m. p. 130°, and forms scaly crystals. A dextro-modification of the same aldehyde has been found in a "false camphor wood."

Thymbra spicata herb from Smyrna gave 1·5% of oil having an odour of thyme and containing 66% carvacrol. It had D^{15} 0·9460, α_D 0°, n_D^{20} 1·50675.

Xanthoxylum alatum fruits gave 3·7% citron-yellow oil, D^{15} 0·8653, α_D −23°35′, n_D^{20} 1·48131, and 0·9% of a crystalline, odourless substance, m. p. 83°, from which a small yield of a *benzoyl* derivative, m. p. 89°, was obtained. The oil appeared to consist mainly of hydrocarbons, and its odour recalled that of phellandrene.

Alpinia galanga oil is lemon-yellow, possesses a pungent, aromatic odour, and shows the following constants: D^{15} 0·9847, α_D +4°20′, n_D^{20} 1·51638, and contains, according to Ultée, pinene, cineol, camphor, and methyl cinnamate.

Gastrochilus pandurata oil resembles estragon and basil oils in odour,

and has D^{15} 0·8746, a_D +10°24′, n_D^{20} 1·48957, ester value 17·3, and is incompletely soluble in 10 vols. of 80% alcohol.

A résumé of recent work on the botany, pharmacology, analysis, and chemistry of essential oils is also given. T. A. H.

Cerebron. IV. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1910, 68, 464—470. Compare Abstr., 1907, i, 168).—Details are given of the preparation of cerebron from ox-brain, and the analysis of various fractions separated by extracting agents. The purest fraction was obtained in crystalline form, and contains C 69·19%, H 11·35%, and N 1·7%. The m. p. is 212—213°. Further work is promised on a second galactoside with which cerebron is usually mixed. W. D. H.

Effect of Alkali on Melanin. ROSS AIKEN GORTNER (*J. Biol. Chem.*, 1910, 8, 341—363).—Alkali in small concentration readily destroys the greater portion of the melanin molecule, the nitrogen falling specially, whilst the carbon and oxygen percentages increase; the sulphur remains practically constant. If the concentration of alkali does not exceed 0·2%, a melanin is extracted from black wool, which is of constant composition, contains no ash, and is readily soluble in acids. W. D. H.

Synergin, the Prochomogen of the Respiration Pigment of Wheat Germs. WLADIMIR PALLADIN (*Biochem. Zeitsch.*, 1910, 27, 442—449).—The prochromogen of wheat, *synergin*, is decomposed by emulsin with production of a chromogen which is oxidised by peroxydase without addition of hydrogen peroxide. The prochromogen is extracted by ethyl and methyl alcohol, and is precipitated by acetone. It is not soluble in ether.

Taka-diastase, like emulsin, decomposes synergin with production of a chromogen which is oxidised by peroxydase. Pepsin is without action.

A number of substances were treated with emulsin and peroxydase in order to ascertain whether pigments are produced. Arbutin yielded a red coloration, less intense than that obtained with the chromogen from wheat, whilst the following compounds gave negative results: aesculetin, amygdalin, apiin, cholesterol, cratægin, cyclamin, digitalin, filicin, galactose, inositol, lecithin, phytin, quercitrin, raffinose, salicin, saligenin, solanine, syringin, and tyrosine.

Synergin is a phosphatide containing a carbohydrate group.

N. H. J. M.

Compounds of Acid Dyes with Various Organic Bases. LEOPOLD RADLBERGER (*Zeitsch. physiol. Chem.*, 1910, 68, 391—394. Compare Abstr., 1908, i, 1001).—By mixing hot aqueous solutions of the components and cooling, the following insoluble or sparingly soluble salts have been obtained. Biguanide sulphate (which crystallises in large plates or in slender needles) yields the *salt*,

$$C_{34}H_{31}O_8N_9S_2,$$

with orange II, and $C_{24}H_{28}O_7N_{12}S_2$ with crystal-ponceau. Acetyl-

guanamine acetate yields an orange *salt*, $C_{20}H_{19}O_4N_7S,2H_2O$ (very hygroscopic when anhydrous), with orange II. C. S.

Causes of the Coloration of Animal Fibres. II. WILHELM SUIDA (*Zeitsch. physiol. Chem.*, 1910, **68**, 381—390. Compare Abstr., 1907, ii, 112).—Having shown that aqueous guanidine hydrochloride yields with picric acid and with crystal-ponceau sparingly soluble, crystalline precipitates, the filtrate containing in the first case all, in the latter 94·2%, of the chlorine, the author uses a reagent prepared by dissolving 5 grams of guanidine hydrochloride and 3 grams of acetic acid in 100 c.c. of water to test the acidity or basicity of a series of dyes which do not give in aqueous solution precipitates with acids alone. The results are: (i) all purely basic, non-sulphonated dyes do not give precipitates; (ii) in dyes which are aminosulphonic acids a decrease of precipitability frequently accompanies an increase in the number of amino- and of sulpho-groups; the generalisation, however, is not always trustworthy; (iii) nearly all of the hydroxyazo-dyes examined (with the exception of eosamine-*B* and azomagenta *G*), and also picric acid and alizarin-red, are more or less quantitatively precipitated, the quantitative course of the reaction being influenced by the number and the position of the hydroxyl and the sulpho-groups; (iv) the precipitation of hydroxy-dyes containing free or alkylated amino-groups is less the greater the number of amino-groups present; (v) whilst tartrazine does not give a precipitate, dyes containing hydroxyl and carboxyl groups, or these and sulpho-groups, give precipitates whether amino-groups are present or not; however, dyes which contain amino- (or alkylated amino-) and carboxyl, but no hydroxyl, groups do not yield precipitates. The outstanding result of the experiments is the important rôle played in the fixing of acid dyes by basic substances, by phenolic hydroxyl and aromatic amino-groups, the carboxyl and sulpho-groups exerting a quite subordinate influence.

Having shown that preliminary treatment of animal fibres with phosphotungstic acid retards the fixation of acidic dyes (*Zeitsch angew. Chem.*, 1909, **22**, 2131), the author has examined the behaviour of the acid towards salts of guanidine. Any soluble salt of guanidine yields with phosphotungstic acid a white precipitate, which is easily soluble in ammonium hydroxide or carbonate; the precipitate remains colourless when boiled with a solution of an acidic dye, but instantly becomes coloured by the addition of a little ammonium hydroxide or carbonate, consequently experiments on guanidine in test-tubes follow quite the same course as those previously performed on animal fibres (*loc. cit.*). Since phosphotungstic acid is an excellent precipitant for the basic fission products of albumins, and since these products frequently contain the group NCN present in guanidine, there can be little doubt that the fixation of acidic dyes by albumins is due to these fission products or the NCN group contained therein; moreover, the chemical compounds formed by acidic dyes with animal fibres are probably constituted in stoichiometric proportions, since Radlberger has shown (Abstr., 1908, i, 1001) that the compounds of guanidine with acidic dyes are thus constituted.

An examination has been made of the behaviour of dyes towards

many substances related to the albumins or their fission products. The results are: (i) all aliphatic or cyclic substances containing the group :N·CO·N: or ·N:C(OH)·N:, such as carbamide, biuret, cyanuric acid, barbituric acid, alloxan, uric acid, theobromine, caffeine, phenylcarbamide, α-phenylhydantoin, glycine anhydride, phenylglycine anhydride, do not yield precipitates with acidic dyes; some of them possessing acidic character (barbituric acid, uric acid, cyanuric acid, ammelide, ammeline) form sparingly soluble compounds with basic dyes; (ii) all derivatives of guanidine with open chains which do not contain substituent acidic groups (aminoguanidine, dicyanodiamide, guanylcarbamide, biguanide, arginine) form sparingly soluble compounds with acidic dyes; (iii) all cyclic compounds containing the guanyl group give sparingly soluble or insoluble compounds with acidic dyes. It is noteworthy that most of the preceding substances which form insoluble or sparingly soluble compounds with acidic dyes are also precipitated by phosphotungstic acid. C. S.

Molecular Weight of Tannin. LEO F. ILJIN (*J. pr. Chem.*, 1910, [ii], **82**, 422—424).—The molecular weight of tannin, purified by the author's processes (Abstr., 1909, i, 503), has been determined by the ebullioscopic method in acetone in MacCoy's modification of Landsberger's apparatus; the values, varying between 1247 and 1637, confirm those of Sabanéeff and of Walden. The author is of opinion that crude tannin contains, in addition to digallic acid and Nierenstein's leucotannin, a not inconsiderable quantity of a complex derivative of gallic acid, for which the name "tannin" should be reserved.

C. S.

δ-ω-Hydroxymethylfurfuraldehyde as the Cause of Some Colour Reactions of Hexoses. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Ber.*, 1910, **43**, 2355—2361. Compare Abstr., 1909, i, 288; this vol., i, 461).—The compound previously described as β-hydroxy-δ-methylfurfuraldehyde is now shown to be the ω-hydroxy-compound, $O<\begin{matrix}C(CHO)\!=\!=\!CH\\ C(CH_2\cdot OH){:}CH\end{matrix}$, as it can be obtained readily from chitose (Fischer and Andreæ, Abstr., 1903, i, 678), and when oxidised yields hydroxymethylpyromucic acid, $O<\begin{matrix}C(CO_2H)\!=\!CH\\ C(CH_2\cdot OH){:}CH\end{matrix}$ (compare Kiermayer, Abstr., 1896, i, 144), identical with the acid prepared by Fischer and Andreae (*loc. cit.*) and by Fenton and Gostling (Trans., 1899, **75**, 429). J. J. S.

ω-Hydroxymethylfurfuraldehyde and its Relationship to Cellulose. ERNST ERDMANN (*Ber.*, 1910, **43**, 2391—2398).—ω-Hydroxymethylfurfuraldehyde (compare Alberda van Ekenstein and Blanksma, preceding abstract) can be prepared from Fenton and Gostling's crude ω-bromomethylfurfuraldehyde (Trans., 1901, **79**, 361, 807) by shaking with aqueous alcoholic silver acetate and extracting with ether. It has b. p. 72°/0·002 mm., and the yield is 5·5 grams from 150 grams of filter paper. It has a pleasant odour, D_4^{23} 1·1022, and gives the usual aldehyde reactions. Its *semioxamazone*, $C_8H_9O_4N_3$,

forms colourless needles, m. p. 216°. When heated under pressure with oxalic acid solution at 134°, it yields an oil from which a *phenylhydrazone*, m. p. 137°, has been isolated. The same phenylhydrazone can be obtained from the oil, b. p. 110°/0·002 mm., formed as a by-product in the preparation of the ω-hydroxymethyl compound. It is suggested that this oil, b. p. 110°/0·002 mm., is identical with the product obtained by Kiermayer from sucrose (Abstr., 1896, i, 144). Its semioxazone is not molten at 260°. J. J. S.

Action of Methyl Sulphate on Dimethylpyrone. ADOLF VON BAEYER (*Ber.*, 1910, **43**, 2337—2343).—Kehrmann and Duttenhöfer's dimethylpyrone methiodide (Abstr., 1906, i, 447) is shown to have the formula $I\cdot O<\substack{CMe\cdot CH\\ CMe:CH}>C\cdot OMe$.

The parent substance, $I\cdot O<\substack{CH\cdot CH\\ CH:CH}>CH$, is termed pyroxonium iodide.

Dimethyl-p-methoxypyroxonium perchlorate, $OMe\cdot C_5H_2Me_2O\cdot ClO_4$, is obtained when dimethylpyrone and methyl sulphate are heated at 50° until the mixture becomes orange-coloured, and the cold product is treated with 20% perchloric acid solution. It is also formed by the action of perchloric acid solution on Kehrmann and Duttenhöfer's iodide. It crystallises from methyl alcohol, is sparingly soluble in cold water, and is resolved into its components when boiled with water for some time. An aqueous solution of ammonium carbonate converts the perchlorate or the iodide into 4-methoxylutidine, the picrate of which melts at 154°, and a solution of sodium acetate or water and magnesium carbonate react with the perchlorate, yielding the *methyl ether* of the enolic form of diacetylacetone, $CH_2Ac\cdot C(OMe):CHAc$, as a colourless oil. J. J. S.

Preparation of Coumarin. FRITZ RASCHIG (D.R.-P. 223684).—The synthetical production of coumarin has been checked by the cost of the salicylaldehyde employed in the usual method of preparation; it is found that this can be replaced by an *o*-tolyl ester containing two atoms of chlorine in the side-chain.

Di-ω-chlorotolyl phosphate (obtained by treating *o*-tolyl phosphate with chlorine at 160—180°) is mixed with anhydrous sodium acetate and heated at about 180° during six hours; the temperature is then raised to 220°, when pure coumarin distils and solidifies in the receiver. The phosphoric acid can be replaced by other acids.

F. M. G. M.

Constitution of α-Pyrocresol. FRANZ ZMERZLIKAR (*Monatsh.*, 1910, **31**, 897—902. Compare Schwarz, Abstr., 1883, 204; Bott, *J.C.S.I.*, 1887, **6**, 646; Bott and Miller, Trans., 1889, **55**, 51).—When α-pyrocresol oxide is fused with potassium hydroxide, the products are *m*-hydroxy-*p*-toluic acid ($Me:OH:CO_2H = 1:3:4$), *m*-hydroxyterephthalic acid, and *m*-cresol.

The formation of these compounds is readily acccounted for on the assumption that α-pyrocresol oxide is 4:2′- or 4:4′-dimethylxanthone,

$C_6H_3Me<\overset{O}{\underset{CO}{}}>C_6H_3Me$; α-pyrocresol itself would then be the corresponding dimethylxanthan, $C_6H_3Me<\overset{O}{\underset{CH_2}{}}>C_6H_3Me$. The identity of synthetical 4 : 4′-dimethylxanthone (Weber, Abstr., 1892, 1093) with α-pyrocresol oxide has been proved, and hence α-pyrocresol is 4 : 4′-dimethylxanthan.
J. J. S.

Preparation of Phenoxozone. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 223367).—The preparation of phenoxozone, m. p. 118—119°, has previously been described (Ullmann and Stein, Abstr., 1906, i, 258); it is now found that it can be prepared in 74% yield by gradually heating sodium *o*-chlorophenoxide to 220° in an iron retort, and subsequently distilling under a pressure of 20—30 mm.
F. M. G. M.

Preparation of Thionaphthen Derivatives from Arylthiolacetic Acids and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 224567).—When arylthiolacetic acids of the type $R\cdot S\cdot CH_2\cdot CO_2R^1$ (where R is a simple or substituted benzene ring, or naphthalene residue, and R^1 hydrogen, a metal, alkyl, or aryl group) are treated with such reagents as phosphoric oxide, zinc, or aluminium chlorides, chlorosulphonic acid, or anhydrous oxalic acid, the following inner condensation take place:

$$S<\overset{CH_2}{\underset{R}{}}\diagdown CO\cdot OR \longrightarrow S<\overset{CH}{\underset{R}{}}>C\cdot OH.$$

This reaction has only been studied previously with phenyl-, *o*- and *p*-tolyl-, and *p*-bromophenyl-thiolacetic acids, but has now been extended to naphthalene derivatives; the products when pure are colourless compounds soluble in alkali, and yielding vat dyes on oxidation.

2-*Hydroxy*-4-*methylthionaphthen* is prepared by heating ethyl *p*-tolylthiolacetate (obtained from thio-*p*-cresol and ethyl chloroacetate) with phosphoric oxide at 100—150°, and separating the product by distillation in steam; it forms long, colourless needles, m. p. 103°.

4-*Chloro*-2-*hydroxythionaphthen*, colourless needles, m. p. 100°, is similarly prepared from *p*-chlorophenylthiolacetic acid (m. p. 107°).

The *compound*, obtained from sodium α-naphthylthiolacetate, when treated with chlorosulphonic acid at 0—5° is yellow, and not volatile in steam.
F. M. G. M.

Substituted Rhodanines and their Condensation Products with Aldehydes. IX. OSKAR ANTULICH (*Monatsh.*, 1910, 31, 891—895).—Ammonium *p*-anisylidenedithiocarbamate, prepared by Losanitsch's method (Abstr., 1907, i, 693), reacts with ethyl chloroacetate, yielding p-*anisidylrhodanine*, $OMe\cdot C_6H_4\cdot N<\overset{CS\cdot S}{\underset{CO\cdot CH_2}{}}$, which crystallises from alcohol in yellow plates, m. p. 153°. The following condensation products have been obtained by the action of a glacial acetic acid solution of an aromatic aldehyde on the rhodanine.

1-p-*Anisidyl*-3-*benzylidenerhodanine*, $OMe\cdot C_6H_4\cdot N<\overset{CS\cdot S}{\underset{CO}{}}>C:CHPh$,

lemon-yellow prisms, m. p. 190°; 1-p-*anisidyl*-3-m-*nitrobenzylidenerhodanine*, $C_{17}H_{12}O_4N_2S_2$, a chrome-yellow, crystalline powder; 1-p-*anisidyl*-3-p-*hydroxybenzylidenerhodanine*, $C_{17}H_{13}O_3NS_2$, yellow needles from acetone, m. p. 258°; 1-p-*anisidyl*-3-p-*dimethylaminobenzylidenerhodanine*, $OMe \cdot C_6H_4 \cdot N<\genfrac{}{}{0pt}{}{CS \cdot S}{CO}>C:CH \cdot C_6H_4 \cdot NMe_2$, orange-red plates, m. p. 219°, and 1-p-*anisidyl*-3-p-*hydroxy*-m-*methoxybenzylidenerhodanine*, $C_{18}H_{15}O_4NS_2$, pale orange-coloured, crystalline powder, m. p. 210°.

J. J. S.

Preparation of Formyl Derivatives of Morphine Alkaloids. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 222920).—The formyl derivatives of the morphine alkaloids are readily obtained by heating either the bases, their salts, or halogen compounds with formic acid or sodium formate, the alcoholic hydroxyl of the base being the point of attack.

Formylcodeine, colourless crystals, m. p. 180°, is prepared by boiling dry codeine with an excess of formic acid (100%) during five or six hours; it is insoluble in water, and sparingly so in alcohol and ether.

Formylmorphine is obtained by boiling together dry morphine hydrochloride (10 parts), sodium formate (5 parts), and formic acid (50 parts). It has m. p. 220° (about), and at 253° decomposes into its progenitors; the *salts* are crystalline. The formyl derivatives of morphine ether and of methylmorphinemethine can be similarly prepared.

F. M. G. M.

Preparation of Morphine Esters of Acylaromatic Hydroxycarboxylic Acids. J. D. RIEDEL (D.R.-P. 224197).—When morphine is treated with the acid chlorides of acylphenolcarboxylic acids, compounds of the type $C_{17}H_{18}O_2N \cdot OCO \cdot R \cdot OR'$ (R = an arylene, R' = an acyl) and of great therapeutic value are produced.

p-*Acetoxybenzoylmorphine*, $C_{26}H_{25}O_6N$, long, prismatic needles sintering at 225°, m. p. 232° (with decomp.), was prepared as follows: p-*Acetoxybenzoic* acid, m. p. 196°, obtained from *p*-hydroxybenzoic acid and acetic anhydride, was treated with phosphorus pentachloride and the mixture distilled in a vacuum, yielding p-*acetoxybenzoyl chloride*, which after distillation at 161—162°/12 mm. solidified to long needles, m. p. 30°. This chloride (dissolved in chloroform) was slowly shaken with morphine in aqueous alkaline solution, the liquids separated, and the product obtained in crystalline form by the addition of ethyl acetate. The *methochloride*, small prisms, was obtained by the action of methyl sulphate and sodium chloride on the base.

p-*Methyl-carbonatobenzoylmorphine*, $C_{26}H_{25}O_7N$, was analogously prepared from *p*-methyl-carbonatobenzoyl chloride (Fischer, Abstr., 1908, 94, i, 892); it forms colourless needles, m. p. 175—176° (with decomp.). The *hydrochloride* crystallises from either methyl or ethyl alcohol in large prisms containing one molecule of the respective alcohol of crystallisation, and with m. p. 165—190° (indefinite). When shaken with the requisite quantity of dilute alcoholic ammonia and kept at the ordinary temperature, the *p*-methyl-carbonato-group is eliminated, and p-*hydroxybenzoylmorphine*, $C_{24}H_{23}O_5N$, m. p. 230—237° (with

decomp.), separates out; the *hydrochloride* forms prismatic needles; the *methobromide*, small leaflets, was prepared by the action of methyl sulphate and potassium bromide in chloroform solution.

F. M. G. M.

Preparation of Halogenhydroxyalkyl-substituted Xanthine Bases. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 224159).—When xanthine bases are treated with substituted halogen alkyloxides, reaction occurs with the iminic hydrogen.

Chlorohydroxypropyltheophylline,

$$\begin{array}{l} \mathrm{NMe{\cdot}CO{\cdot}C{-\!\!-}N{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl} \\ \mathrm{CO{\cdot}NMe{\cdot}C{\cdot}N{:}CH} \end{array},$$

m. p. 141—143°, is prepared by heating theophylline with epichlorohydrin in a closed vessel at 130° during several hours with continual stirring; it is readily soluble in water, and when boiled with an alkaline hydroxide is converted into dihydroxypropyltheophylline.

F. M. G. M.

Strychnine Alkaloids. IX. Derivatives of Strychninesulphonic Acid I. and Oxidation of Bromostrychnine. HERMANN LEUCHS and PAUL BOLL (*Ber.*, 1910, **43**, 2362—2374. Compare Abstr., 1909, i, 120, 671).—The sulphonic acid group of strychninesulphonic acid is not attached to one of the benzene nuclei, and hence the acid readily yields substitution products, for example, mono- and di-chloroderivatives, a monobromo-, a nitro- and a nitrobromo-derivative. Strychnine itself yields a hydrate of a dinitro-derivative, and it is probable that one of the nitro-groups of this derivative occupies the same position as the sulphonic group in strychninesulphonic acid. The nitrosulphonic acid is readily reduced to the corresponding amino-acid, and with alkaline reducing agents, azostrychninesulphonic acid is also formed. So far it has not been found possible to prepare diazo- and hydroxy-compounds corresponding with the amino-derivative. The sulphonic acid group of strychninesulphonic acid is not removed by heating with concentrated hydrochloric acid, but an atom of chlorine is introduced: $C_{21}H_{22}O_5N_2S + HCl = C_{21}H_{21}O_4N_2SCl + H_2O$, and this chloro-acid when boiled with water loses hydrogen chloride, yielding a product isomeric with the original sulphonic acid and termed *iso*strychninesulphonic acid I. The authors do not agree with the conclusion that the bromine atom in bromostrychnine is attached to a carbon atom of a side-chain (Abstr., 1885, 911; Ciusa and Scagliarina, this vol., i, 583.)

Nitrostrychninesulphonic acid I., $C_{21}H_{21}O_7N_3S$, prepared by boiling the base for a short time with $5N$-nitric acid in the presence of carbamide, crystallises in massive, straw-yellow prisms, which are not molten at 300°. It has $[\alpha]_D^{20}$ −364° in dilute sodium hydroxide solution. The corresponding *amino*-acid, $C_{21}H_{23}O_5N_3S$, crystallises in colourless needles or thin plates, and decomposes at 270°. Its solution in sodium hydroxide has $[\alpha]_D^{20}$ −244·8°. The *hydrochloride*,

$$C_{21}H_{23}O_5N_3S,HCl,$$

and sulphate are readily soluble, but the nitrate sparingly soluble. *Azostrychninesulphonic acid I.*, $C_{42}H_{42}O_{10}N_6S_2$, crystallises in orange-

yellow plates containing $8H_2O$, and when dehydrated under reduced pressure at 80° forms greenish-yellow crystals.

Bromostrychninesulphonic acid I., $C_{21}H_{21}O_5N_2SBr$, prepared by the action of a solution of bromine in hydrobromic acid (D 1·46) on the sulphonic acid, forms colourless, rectangular prisms or plates. In aqueous sodium hydroxide solution it has $[\alpha]_D^{20}$ – 233·6°.

Bromonitrostrychninesulphonic acid, $C_{21}H_{20}O_7N_3SBr,H_2O$, formed by the action of bromine on the nitro-acid, crystallises in broad, yellow needles. Care is required in the preparation, as there is a tendency for the bromine to replace the nitro-group.

Chlorostrychninesulphonic acid I., $C_{21}H_{21}O_5N_2SCl,H_2O$, is formed by the action of chlorine water and concentrated hydrochloric acid on the sulphonic acid at 0°, and crystallises in massive, six-sided prisms with $[\alpha]_D^{20}$ – 239·9°. *Dichlorostrychninesulphonic acid I.*,

$$C_{21}H_{20}O_5N_2SCl_2,H_2O,$$

forms six-sided plates and has $[\alpha]_D^{20}$ – 155·9°.

Chloride of *isostrychninesulphonic anhydride*, $C_{21}H_{21}O_4N_2SCl,2H_2O$, obtained by the action of concentrated hydrochloric acid on the sulphonic acid at 130—135°, crystallises in long prisms, loses its water of hydration at 80° under reduced pressure, and gives Otto's strychnine reaction. iso*Strychninesulphonic acid I*, $C_{21}H_{22}O_5N_2S,2H_2O$, has $[\alpha]_D^{20}$ – 242° to – 244° in alkaline solution, and is not so readily soluble in water as the isomeric acid. The *chloride* of iso*nitrostrychninesulphonic anhydride I.*, $C_{21}H_{20}O_6N_3SCl$, crystallises in irregular plates, practically insoluble in water, and iso*nitrostrychninesulphonic acid I.*, $C_{21}H_{21}O_7N_3S$, has $[\alpha]_D^{20}$ – 285·9°, and its solubility in water is 1 in 2000.

When oxidised with hydrogen peroxide, the sulphonic acid I. yields the *amino-oxide*, $C_{21}H_{22}O_6N_2S,2H_2O$, in the form of long, colourless needles, with $[\alpha]_D^{20}$ – 101·8° in alkaline solution. It is readily reduced by sulphurous acid. The nitrosulphonic acid I. when oxidised in a similar manner yields the *amino-oxide*, $C_{21}H_{21}O_8N_3S$, as massive, yellow needles, with $[\alpha]_D^{20}$ – 240°.

Bromostrychninonic acid, $C_{21}H_{19}O_6N_2Br$, prepared by oxidising bromostrychnine (Beckurts, Abstr., 1890, 1329) in acetone solution with permanganate, crystallises in twinned needles, is hydrated, has m. p. 274—276° (corr.), and $[\alpha]_D^{20}$ – 54·8° in alkaline solution. J. J. S.

Strychnine Alkaloids. X. Reactions of Strychninonic Acid and of Strychninolone. HERMANN LEUCHS and PAUL REICH (*Ber.*, 1910, 43, 2417—2429. Compare Abstr., 1908, i, 564; 1909, i, 602). —Attempts have been made to prove the presence of two carboxylic groups in strychninonic acid. With methyl alcohol and hydrogen chloride a monomethyl ester is formed, and ultimately products containing chlorine, and these with sodium carbonate yield two substances, one containing two carbomethoxy-groups and the other a carboxylic and a carbomethoxy-group, but both derived from the original acid plus a molecule of water, so that it is possible that the second carboxylic group is formed by the addition of water to an :N·CO· group in the original strychninonic acid molecule.

The acid reacts with dilute hydrochloric acid, yielding two hydrates containing respectively one and two molecules of water. The former

is regarded as an imino-acid formed by the rupture of the $\begin{array}{l}:N\\ \ \vert\\ \cdot CO\end{array}$ group. In the other, the second molecule of water is probably attached to the carbonyl group.

An anilide is formed when the acid is boiled with aniline, and hence the carbonyl group is in all probability not in the α-position with respect to the carboxylic group.

Methyl strychninonate, $C_{22}H_{22}O_6N_2$, crystallises from methyl alcohol in brilliant prisms, m. p. 247—249°. A *hydrate* of the methyl ester, $C_{22}H_{24}O_7N_2$, is formed when the solution in methyl alcohol is saturated with hydrogen chloride, and crystallises in rectangular prisms or plates, m. p. 184—186°. It dissolves in both dilute acids and dilute alkalis. The *dimethyl ester hydrate* forms a platinichloride, probably $C_{46}H_{54}O_{14}N_4PtCl_6$.

Strychninonic acid hydrate, $C_{21}H_{22}O_7N_2$, crystallises from water in long needles containing $2H_2O$, which it loses at 105°, and then has m. p. 270—275° (decomp.). It has $[\alpha]_D^{20}$ $+39{\cdot}6°$. The *dihydrate*,

$$C_{21}H_{24}O_8N_2,H_2O,$$

is less soluble in water, and crystallises at 0° in rectangular prisms; it has m. p. 235—240°. It yields a *sodium* salt, $C_{21}H_{23}O_8N_2Na$, which forms small prisms, m. p. 250—255° (decomp.).

Nitrostrychninonic acid, $C_{21}H_{19}O_8N_3$, obtained by the action of 5*N*-nitric acid and carbamide on strychninonic acid and extracting with chloroform, crystallises from glacial acetic acid in six-sided plates, m. p. 264—266° (decomp.). Yield, 20—25%.

Strychninonanilide, $C_{27}H_{25}O_5N_3$, crystallises from 75% acetic acid in short, massive prisms, m. p. 255° (decomp.).

Strychninolone contains a hydroxyl group, and yields an *acetyl* derivative, $C_{21}H_{20}O_4N_2$, which crystallises from methyl alcohol in brilliant prisms, m. p. 126—128° (decomp.). With a chloroform solution of phosphoryl chloride, strychninolone yields *strychninolone chloride hydrate*, $C_{19}H_{19}O_3N_2Cl$, which crystallises from absolute alcohol in slender needles, m. p. 236°.

When heated with concentrated hydrochloric acid at 100°, strychninolone yields two hydrates. The *hydrochloride* of *hydrate I*,

$$C_{19}H_{21}O_4N_2Cl,$$

crystallises from hot water in glistening prisms, m. p. 305—310° (decomp.). The hydrate itself is a syrup. The *hydrate II*,

$$C_{19}H_{20}O_4N_2,4H_2O,$$

crystallises from water in thick prisms or long needles, m. p. 239—240°. Both hydrates have the properties of amino-acids.

J. J. S.

Glutamic Acid and Pyrrolidonecarboxylic Acid. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1910, **68**, 487—503. Compare this vol., i, 230).—Owing to the ease with which it changes into glutamic acid, the formation of pyrrolidonecarboxylic (not pyrrolidinecarboxylic, *loc. cit.*) acid has not yet been detected amongst the products of the hydrolysis of albumins by the ordinary processes. With this end in view, the authors have instituted further experiments for the separation of pyrrolidonecarboxylic acid from

other amino-acids, especially from glutamic acid. Utilising the amino-group in the latter, the authors have converted it by means of ethyl chloroformate into *carbethoxyglutamic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO_2Et,$$

which forms a *barium* salt, $C_8H_{11}O_6NBa,H_2O$, a *silver* salt,

$$C_8H_{11}O_6NAg_2,$$

and an amorphous, green *copper* salt, $C_8H_{11}O_6NCu$, which is much less soluble in water than copper pyrrolidonecarboxylate. It is noteworthy that glutamic acid, owing to the influence of the amino-group on the neighbouring carboxyl, behaves generally like a monobasic acid (*loc. cit.*), whereas carbethoxyglutamic acid exerts its dibasic function in salt formation. The separation of glutamic acid from pyrrolidonecarboxylic acid is very conveniently effected by Siegfried's carbamino-reaction (Abstr., 1906, i, 144).

The formation of pyrrolidonecarboxylic acid from glutamic acid by heating has been examined more thoroughly. At 150—160°, *d*-glutamic acid yields a product, m. p. about 145°, $[\alpha]_D$ $-10{\cdot}06°$ in water, from which *l*-pyrrolidonecarboxylic acid, $[\alpha]_D$ $-11{\cdot}5°$, can be separated by fractional crystallisation from water. At 180—220°, *d*-glutamic acid yields chiefly *i*-pyrrolidonecarboxylic acid. At 160—170°, under conditions as yet unknown, *d*-glutamic acid yields occasionally a small quantity of a *substance*, $C_5H_7O_3N$, m. p. 180—182°, $[\alpha]_D$ $+4{\cdot}24°$ in water. A *l*-pyrrolidonecarboxylic acid, obtained from *d*-glutamic acid and having $[\alpha]_D$ $-11{\cdot}27°$ in water, had $[\alpha]_D$ $+4{\cdot}24°$ in methyl alcohol and $+3{\cdot}75°$ in ethyl alcohol. A *l*-pyrrolidonecarboxylic acid, $[\alpha]_D$ $-9{\cdot}38°$ (therefore containing about 19% of the inactive acid), was treated with 5*N*-hydrochloric acid for six to seven days, whereby *d*-glutamic acid, $[\alpha]_D$ 23·3°, was obtained; pure *d*-glutamic acid in 5*N*-hydrochloric acid has $[\alpha]_D$ $+28{\cdot}88°$. Under similar conditions, *i*-pyrrolidonecarboxylic acid yielded *i*-glutamic acid hydrochloride, m. p. 200°.

Silver glutamate, $C_5H_7O_4NAg_2$, *basic zinc glutamate*,

$$(C_5H_8O_4N)_2Zn,ZnO,$$

and the *lead*, *copper*, and *silver* salts of pyrrolidonecarboxylic acid are described. C. S.

Existence of Liquid Racemic Compounds. ALBERT LADENBURG and SOBECKI (*Ber.*, 1910, **43**, 2374—2380).—The freezing-point curve of mixtures of *d*- and *l*-pipecolines has been determined; the curve shows two eutectics at $-6{\cdot}65°$ and a maximum at $-4{\cdot}9°$, corresponding with the formation of a definite racemic compound.

The solubility of dipentene in 98·99% acetic acid at 12° has been determined, the method of estimation being conversion into bromide. The saturated solution of dipentene in acetic acid when shaken with 10% of *d*-limonene still shows the same amount of hydrocarbon in solution, although the solution has become strongly dextrorotatory. The two results are contradictory, but the authors conclude that dipentene is a mixture and not a definite compound.

Experiments have also been made on the solubility of *dl*-ethylpiperidine and mixture of *dl*- with *l*-ethylpiperidine in water at 24·95° and 21·95°. The concentration of the solutions was determined by means of standard hydrochloric acid, using *o*-nitrophenol as

indicator. The results show that the solubility is not affected by the presence of an excess of one of the active constituents. The solution, however, was lævorotatory.

Pure *l*-α-ethylpiperidine is best prepared by resolution of the *dl*-base with Reychler's acid. The *l*-base has D^{23} 0·8451, and $[\alpha]_D$ $-21·3°$.

Details of the preparation of the *dl*-base are given. J. J. S.

Anomalous Products of Benzoylation. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1910, **43**, 2574—2581).—After quoting several instances in which anomalous products are obtained by benzoylation in pyridine or quinoline (Heller and Fiesselmann, Abstr., 1902, i, 779; Heller, Abstr., 1903, i, 827; Scholl and Berblinger, Abstr., 1907, i, 257), the authors describe the following benzoylated substances containing pyridine. By treating a cold pyridine solution of *p*-aminobenzoic acid with benzoyl chloride, the *substance*, $2C_{14}H_{11}O_3N,C_5NH_5$, m. p. above 340°, is obtained, which crystallises in slender needles, forms sparingly soluble *sodium* and *potassium* salts, and retains the pyridine even after steam has been passed through its strongly alkaline solution; the pyridine is removed, however, by hydrochloric acid at 170°, aniline and *p*-aminobenzoic acid being formed. Benzoylation in quinoline or dimethlaniline yields only the normal product. In a similar way, *m*-aminobenzoic acid and *p*-aminophenylacetic acid yield respectively the *substances*, $2C_{14}H_{11}O_3N,C_5NH_5$ and

$$2C_{15}H_{13}O_3N,C_5NH_5$$

(which are precipitated by the addition of dilute hydrochloric acid), together with the normal products of benzoylation. When *p*-benzoylaminobenzoic acid is heated with acetic anhydride, an *isomeride* separates on cooling in tufts of colourless needles; it contains $\frac{1}{4}Ac_2O$, which is removed at 150°, but not by sodium carbonate solution, and has m. p. 240° (softening at 150—155° and resolidifying). The dried substance sinters at 265°, resolidifies, and then slowly decomposes at a much higher temperature; it is not immediately soluble in boiling sodium carbonate, and only dissolves slowly in warm sodium hydroxide, the solution yielding *p*-benzoylaminobenzoic acid by acidification. On account of these properties, the isomeride receives the constitution $C_6H_4{<}\begin{matrix}NH_2Bz\\ \text{—}CO\text{—}\end{matrix}{>}O$, and is called p-*benzoylaminobenzoic acid cycloid.* When boiled with acetic anhydride, *p*-acetylaminobenzoic acid yields p-*diacetylaminobenzoic anhydride,* $(NAc_2·C_6H_4·CO)_2O$, m. p. 253—254°.

The paper also contains a reply to the statements of Bamberger (Abstr., 1909, i, 509) and of Mohr (this vol., i, 116) that acetylanthranil contains the 1 : 3-oxazine ring. C. S.

Constitution of Benzoylanthranil. OTTO MUMM and HUGO HESSE (*Ber.*, 1910, **43**, 2505—2511).—Two formulæ have been proposed for benzoylanthranil: that of Friedländer and Wleügel (I), and that of Angeli and Angelico (II), of which the latter is considered the

$$C_6H_4{<}\begin{matrix}N·CO·C_6H_5\\ |\\ CO\end{matrix} \qquad\qquad C_6H_4{<}\begin{matrix}N{=}CPh\\ \quad\;\;|\\ CO{-}O\end{matrix}$$

(I.) (II.)

more probable. No direct proof of its validity, however, has yet been given, but such is now afforded by the interaction of anthranilic acid with benzanilideiminochloride to form a ring system. From the intermediate product of the reaction, water must be eliminated if the Friedländer-Weiügel formula is correct, and aniline must be eliminated if the Angeli-Angelico formula is the true one. Experiments in absolute ethereal solution, with or without pyridine, proved that aniline is eliminated and benzoylanthranil formed.

Diphenylquinazolone, $C_6H_4<\begin{matrix} N = CPh \\ CO \cdot NPh \end{matrix}$, could not be obtained by the action of benzanilide chloride on anthranil, but it was obtained by shaking sodium anthranilate in aqueous solution with benzanilide-iminochloride in ether. It crystallises in prisms, m. p. 158—159°, and has faintly basic properties, the *hydrochloride* having m. p. 172°.

E. F. A.

Preparation of Substituted Indoles by the Catalytic Decomposition of Arylhydrazones. ALEXANDER E. ARBUSOFF and W. M. TICHWINSKY (*Ber.*, 1910, **43**, 2301—2303).—The phenyl- and tolyl-hydrazones of the lower aliphatic aldehydes and ketones yield substituted indoles when heated with small amounts (0·1 gram) of cuprous chloride at 180—230°. The bases can be isolated by subjecting the crude products to fractional distillation under reduced pressure.

2 : 3-Dimethylindole, 3-methylindole, and 3 : 5-dimethylindole have been prepared from methyl ethyl ketone phenylhydrazone, propaldehyde-phenylhydrazone, and propaldehyde-*p*-tolylhydrazone respectively.

Zinc chloride and platinous chloride can be used instead of cuprous chloride.

J. J. S.

Syntheses with *o*-Xylylene Bromide. MAX SCHOLTZ and R. WOLFRUM (*Ber.*, 1910, **43**, 2304—2318. Compare Scholtz, Abstr., 1898, i, 305, 383, 471, 565, 567).—*tert.*-Butylamine reacts with *o*-xylylene bromide in the same manner as other aliphatic primary amines, no steric hindrance is observable, and the product is tert.-*butyldihydroisoindole*, $C_6H_4<\begin{matrix} CH_2 \\ CH_2 \end{matrix}>N \cdot CMe_3$, which crystallises from ethyl alcohol in glistening plates, m. p. 42° and b. p. 125—130°/13 mm. Its *methiodide*, $C_{13}H_{20}NI$, forms colourless crystals, m. p. 221°.

p-Aminoacetophenone (3 mols.) also condenses with *o*-xylylene bromide (1 mol.), yielding p-*acetylphenyldihydroisoindole*,

$$C_6H_4<\begin{matrix} CH_2 \\ CH_2 \end{matrix}>N \cdot C_6H_4 \cdot COMe,$$

in the form of glistening plates, m. p. 197°. This compound condenses with aldehydes in the presence of alkalis in much the same manner as *p*-aminoacetophenone itself (Scholtz and Huber, Abstr., 1904, i, 253).

The *benzylidene* derivative, $C_8H_8\colon N \cdot C_6H_4 \cdot CO \cdot CH\colon CHPh$, crystallises from alcohol in glistening, yellow plates, m. p. 202°; the *cinnamylidene* derivative, $C_8H_8\colon N \cdot C_6H_4 \cdot CO \cdot CH\colon CH \cdot CH\colon CHPh$, crystallises from

acetone in slender, orange-coloured needles, m. p. 187°; the *nitrobenzylidene* derivative, $C_{23}H_{18}O_3N_2$, forms a pale yellow, crystalline powder, m. p. 238°. 2 p'-*Dimethylamino*-p-*cinnamoylphenyldihydroisoindole*, $C_8H_8:N\cdot C_6H_4\cdot CO\cdot CH:CH\cdot C_6H_4\cdot NMe_2$, crystallises from pyridine in golden-yellow plates, m. p. 196°.

At 100° 2-phenyldihydro*iso*indole combines readily with methyl iodide, yielding the *methiodide*, $C_8H_8:NPh,MeI$, which forms colourless plates, m. p. 177°. 2-Phenyldihydro*iso*indole condenses readily with aldehydes, especially in the presence of concentrated hydrochloric acid, yielding derivatives of diphenylmethane, or, in the case of aromatic aldehydes, derivatives of triphenylmethane. The condensation takes place in the para-position with respect to the nitrogen atom, as *p*-tolyldihydro*iso*indole does not react with aldehydes. Formaldehyde reacts without the aid of a condensing reagent, yielding *bisxylyleneaminodiphenylmethane*, $CH_2(C_6H_4\cdot N:C_8H_8)_2$, which forms slender needles, m. p. 308—309°. *Bisxylyleneaminotriphenylmethane*, $CHPh(C_6H_4\cdot N:C_8H_8)_2$, separates from a mixture of pyridine and alcohol in colourless, felted needles, m. p. 265°. *Bisxylyleneaminodimethylaminotriphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH(C_6H_4\cdot N:C_8H_8)_2$, crystallises from pyridine in colourless needles, m. p. 185°. *Bisxylyleneaminodiphenylstyrylmethane*, $CHPh:CH\cdot CH(C_6H_4\cdot N:C_8H_8)_2$, forms a yellow, crystalline powder, which is not molten at 300°. *Bisxylyleneamino-di-*m*-tolylmethane*, $CH_2(C_6H_3Me\cdot N:C_8H_8)_2$, obtained from *m*-tolyldihydro*iso*indole, crystallises from pyridine in colourless needles, m. p. 255°.

Scholtz and Jaross (Abstr., 1901, i, 485) have shown that secondary 1 : 4-diamines condense with alcoholic solutions of aldehydes without the use of a condensing agent; an exception to this rule is xylylene-di-*o*-toluidine, which does not react. It is now shown that this base will condense with aldehydes in the presence of concentrated hydrochloric acid. With formaldehyde, it yields *methylene-di-*o*-tolyl-*o*-xylylenediamine*, $C_6H_4<\begin{matrix}CH_2\cdot N(C_6H_4Me)\\CH_2\cdot N(C_6H_4Me)\end{matrix}>CH_2$, as glistening prisms, m. p. 139°, and with benzaldehyde, *benzylidene-di-*o*-tolyl-*o*-xylylenediamine*, $C_6H_4<\begin{matrix}CH_2\cdot N(C_6H_4Me)\\CH_2\cdot N(C_6H_4Me)\end{matrix}>CHPh$, m. p. 180°.

Methylamine reacts with xylylenepiperidonium bromide at 200° in much the same manner as ammonia (Abstr., 1898, i, 567), yielding *pentamethylenemethylxylylenediamine*,

$$C_6H_4<\begin{matrix}CH_2\cdot NMe\cdot CH_2\cdot CH_2\\CH_2\cdot NH-CH_2\cdot CH_2\end{matrix}>CH_2.$$

This is a colourless liquid, b. p. 160—165°/15 mm., and yields a *benzenesulphonyl* derivative, $C_{14}H_{21}N_2\cdot SO_2Ph$, m. p. 87°. When distilled, the methyl derivative yields 2-methyldihydro*iso*indole (Fränkel, Abstr., 1901, i, 45).

The products obtained by the condensation of xylylenepiperidonium bromide with aliphatic secondary amines, and previously represented as $NR_2\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot N:C_5H_{10}$, are undoubtedly cyclic compounds of the type $C_6H_4<\begin{matrix}CH_2\cdot NR\cdot CH_2\cdot CH_2\\CH_2\cdot NR\cdot CH_2\cdot CH_2\end{matrix}>CH_2$. Aromatic primary amines react with xylylenepiperidonium bromide in different ways,

according to the nature of the amine. With aniline at 200°, piperidine and phenyldihydro*iso*indole are formed; *p*-toluidine reacts in a similar manner, but *o*-toluidine does not yield an *iso*indole derivative. The reaction probably consists of a rupture of the original ring, the formation of an eleven-membered ring, and the splitting up of this into the two compounds mentioned.

Dixylyleneammonium bromide (Scholtz, Abstr., 1891, 1353) when heated with piperidine and water at 200° yields a ditertiary base,

$$C_6H_4{<}^{CH_2}_{CH_2}{>}N\cdot CH_2\cdot C_6H_4\cdot CH_2.C_5NH_{10},$$

xylylenepentamethylenexylylenediamine, b. p. 240—245°.

o-Xylylene bromide and tetrahydroquinoline condense in the usual manner, yielding o-*xylylenetetrahydroquinolonium bromide*,

$$C_6H_4{<}^{CH_2}_{CH_2}{>}NBr{:}C_9H_{10},$$

which is a syrup; the corresponding *iodide*, $C_{17}H_{18}NI$, forms colourless needles, m. p. 238°, and the *picrate*, $C_{17}H_{18}N\cdot O\cdot C_6H_2(NO_2)_3$, yellow needles, m. p. 165°.

Dibenzyl-o-*xylyleneammonium bromide*, $C_8H_8{:}NBr(CH_2Ph)_2$, prepared from *o*-xylylene bromide and dibenzylamine in chloroform solution, crystallises in snow-white plates, m. p. 188°, and when heated with ammonia at 200° yields *dibenzyl*-o-*xylylenediamine*,

$$C_6H_4(CH_2\cdot NH\cdot CH_2Ph)_2,$$

the *hydrochloride* of which has m. p. 251°.

o-*Xylylenedi*iso*amylammonium bromide* is an oil; the *iodide*, $C_{18}H_{30}NI$, crystallises from water, and has m. p. 139°. The bromide when heated with ammonia at 200° yields o-*xylylenedi*iso*amyldiamine*, $C_6H_4(CH_2\cdot NH\cdot C_5H_{11})_2$, a colourless oil with b. p. 210°/12 mm.

Dibenzylpiperidonium bromide, $C_5H_{10}{:}NBr(CH_2Ph)_2$, prepared by the action of dibenzylamine on $\alpha\epsilon$-dibromopentane, crystallises in colourless plates, m. p. 253°, and when heated with ammonia at 200° yields benzylamine, dibenzylamine, and benzylpiperidine. o-*Xylylenedipropylammonium bromide*, $C_8H_8{:}NBr(C_3H_7)_2$, crystallises in colourless plates, m. p. 107°, and when heated with ammonia at 200° yields propyl bromide and 2-*propyldihydro*iso*indole*. The latter is a colourless oil, b. p. 230—240°, and forms a *methiodide*, $C_{11}H_{15}N,MeI$, m. p. 150°. The *platinichloride*, $(C_{11}H_{15}N)_2H_2PtCl_6$, forms a reddish-yellow powder, m. p. 192°. The decomposition of the dipropyl derivative is thus analogous to that of the diethyl salt (Abstr., 1898, i, 568).

2-*Amylenedihydro*iso*indole*, $C_8NH_8\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$, obtained by treating xylylenepiperidonium bromide with moist silver oxide, evaporating to a syrup, and distilling, has b. p. 140—150°/12 mm. Its *methiodide* is also oily. J. J. S.

New Method for the Synthesis of *iso*Quinoline Bases. AMÉ PICTET and ALFONS GAMS (*Ber.*, 1910, **43**, 2384—2391. Compare Abstr., 1909, i, 671).—Acylated carbinols of the type

$$OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot R,$$

where R = methyl, phenyl or benzyl, readily undergo condensation when heated with phosphoric oxide and xylene, yielding 1-substituted

*iso*quinolines. Phenylformylaminomethylcarbinol reacts in a similar manner, yielding *iso*quinoline, and this is the most convenient synthetical method for the preparation of the base.

Phenylphenacetylaminomethylcarbinol,

$$OH\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot CH_2Ph,$$

obtained by reducing ω-phenylacetylaminoacetophenone (Robinson, Trans., 1909, **95**, 2167) with sodium amalgam, alcohol, and acetic acid, crystallises from water in slender needles, m. p. 123°.

Phenylbenzoylaminomethylcarbinol (Kolshorn, Abstr., 1904, i, 675) is prepared most readily by reducing benzoylaminoacetophenone (Robinson, *loc. cit.*). *Phenylacetylaminomethylcarbinol*,

$$OH\cdot CHPh\cdot CH_2\cdot NHAc,$$

crystallises from benzene in colourless needles, m. p. 104°. 1-Benzyl*iso*quinoline forms colourless needles, m. p. 56°. 1-*Phenyl*iso*quinoline*, $C_{15}H_{11}N$, crystallises from dilute alcohol in colourless needles, m. p. 93°, b. p. 298°/729 mm. The *hydrochloride* has m. p. 235—236°; the *picrate*, m. p. 164·5°, and the *platinichloride* forms red needles, m. p. 242° (decomp.).

1-*Methyl*iso*quinoline*, $C_{10}H_9N$, is a colourless oil, b. p. 243—245°/728 mm. The *hydrochloride* forms colourless needles, m. p. about 170°; the *sulphate* forms colourless prisms, m. p. 245°; the *picrate* has m. p. 206—208°; the *dichromate* forms red prisms, sparingly soluble in water, and decomposes at about 150°; the *platinichloride*,

$$2C_{10}H_9N,H_2PtCl_6,2H_2O,$$

forms reddish-yellow prisms, and melts at 201·5° when anhydrous. The base is probably identical with the two methyl*iso*quinolines described in Beilstein.

ω-*Formylaminoacetophenone*, $COPh\cdot CH_2\cdot NH\cdot CHO$, prepared by the action of crystallised formic acid on ω-aminoacetophenone hydrochloride, crystallises from a mixture of benzene and light petroleum in large, flat prisms, m. p. 70—71°, and when reduced with sodium amalgam, alcohol, and formic acid yields *phenylformylaminomethylcarbinol*, $OH\cdot CHPh\cdot CH_2\cdot NH\cdot CHO$, as a reddish-brown, crystalline mass. J. J. S.

Preparation of a Dihydroxycarbazoledisulphonic Acid. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224952).—The product obtained by fusing carbazoledisulphonic acid with an alkali hydroxide has been described (Schultz and Hauenstein, Abstr., 1907, i, 1074), but whether the product was a dihydroxy- or a hydroxycarbazolesulphonic acid is not definitely stated.

When carbazole is treated with fuming sulphuric acid (five parts) at a temperature not exceeding 40°, and then slowly heated to 100°, disulphonation takes place; if this mixture is further treated with two parts of sulphuric acid (containing 65% SO_3) and kept at 90—100° until the product ceases to be separable on the addition of salt, *carbazoletetrasulphonic acid* is obtained, and finally isolated by evaporation in the form of its *potassium* salt.

Dihydroxycarbazoledisulphonic acid is prepared from the foregoing acid by fusion with alkali hydroxide at a temperature of 240—300°;

the *potassium* salt forms colourless needles containing $4H_2O$, and shows a green fluorescence on addition of ammonium hydroxide.

The free acid can be isolated from its *barium* salt.

F. M. G. M.

[Preparation of *N*-Alkyl- and of *N*-Aryl-carbazoles and their Indophenol Derivatives.] LEOPOLD CASSELLA & Co. (D.R.-P. 224951).—The *N*-alkyl-carbazoles have been previously described; it is now found that *N*-aryl-carbazoles can be prepared in analogous manner, and that they likewise, when heated with polysulphides, yield valuable dyes.

9-*Benzylcarbazole*, colourless needles, m. p. 118—120°, is prepared by the action of benzyl chloride on potassium carbazole at high temperatures or under pressure.

9-*Phenylcarbazole* is obtained by heating potassium carbazole with bromobenzene in the presence of copper powder under pressure at a temperature of 180—220°; it forms colourless needles, m. p. 82—84°.

9-p-*Tolylsulphonylcarbazole*, pale yellow needles, m. p. 127—128°, is prepared from potassium carbazole and *p*-toluenesulphonyl chloride. These substances combine with *p*-nitrosophenol, yielding dark blue powders, which on reduction form greyish-white, crystalline leuco-compounds.

F. M. G. M.

Condensation Products from Salicylidene- and Hydrocyano-salicylidene-aniline (Anilino-*o*-hydroxyphenylacetonitrile). GEORG ROHDE and G. SCHÄRTEL (*Ber.*, 1910, **43**, 2274—2286).—Miller and Plöchl (*Ber.*, 1896, **27**, 1730; 1898, **29**, 2699) have shown that Schiff's bases do not undergo the benzoin condensation with potassium cyanide. The product obtained by Schwab (Abstr., 1901, i, 380) by condensing *o*-hydroxybenzylideneaniline with an alcoholic solution of potassium cyanide is shown to be 4-cyano-3-phenyl-2-*o*-hydroxyphenyl-3 : 4-dihydro-1 : 3-benzoxazine, $C_6H_4<\begin{matrix}O\text{———}CH\cdot C_6H_4\cdot OH \\ CH(CN)\cdot NPh\end{matrix}$, and not to have the constitution ascribed to it by Schwab. The product is prepared most readily by shaking vigorously for three hours an alcoholic solution of aniline (1 mol.) and salicylaldehyde (2 mols.) with an alcoholic solution of potassium cyanide (1 mol.). When its ethereal solution is hydrolysed with concentrated hydrochloric acid, the products are salicylaldehyde and the acid amide hydrocyanosalicylideneaniline, *anilino-o-hydroxyphenylacetamide*, $OH\cdot C_6H_4\cdot CH(NHPh)\cdot CO\cdot NH_2$, which yields a *hydrochloride*, $C_{14}H_{14}O_2N_2,HCl$, crystallising from alcohol in colourless needles, m. p. 183°. The amide crystallises from benzene in colourless needles containing benzene and melting at 63°; when further heated, it gives up benzene, solidifies, and then has m. p. 126° The same amide can be prepared by adding Miller and Plöchl's hydrocyanosalicylideneaniline (anilino-*o*-hydroxyphenylacetonitrile) to concentrated hydrochloric acid.

Schwab's condensation product can be synthesised by shaking an alcoholic solution of hydrocyanosalicylideneaniline with salicylaldehyde and potassium hydroxide dissolved in a little water. The following derivatives are described: *Sodium* salt, $C_{21}H_{15}O_2N_2Na$, yellow,

glistening powder, m. p. 249°, obtained by shaking an ethereal solution of the 1 : 3-benzoxazine with 10% sodium hydroxide solution; *benzoyl* derivative, $C_{28}H_{20}O_3N_2$, yellow crystals, m. p. 188°; *benzenesulphonyl* derivative, $C_{27}H_{20}O_4N_2S$, glistening needles from alcohol, m. p. 162°.

Hydrocyanosalicylideneaniline and benzaldehyde undergo condensation in the presence of potassium hydroxide, yielding *4-cyano 2 : 3-diphenyl-2 : 4-dihydro-1 : 3-benzoxazine*, $C_6H_4<\begin{matrix}O\text{———}CHPh\\ CH(CN)\cdot NPh\end{matrix}$, in the form of yellow needles, m. p. 138°.

When molecular quantities of salicylideneaniline and potassium cyanide are condensed, a *product*, $C_{14}H_{12}ON_2$, is formed, which crystallises from benzene in compact prisms, m. p. 135—137°. The same product is formed by condensing salicylaldehyde and salicylideneaniline with potassium cyanide or salicylidene-aniline and hydrocyanosalicylideneaniline with potassium cyanide. It is isomeric with hydrocyanosalicylideneaniline, from which it can be obtained by shaking with potassium cyanide, potassium carbonate, or sodium ethoxide solutions.

A by-product formed in the preparation of the benzoxazine separates as dark red needles from the mother liquors after a time, and can be obtained most readily by boiling an alcoholic solution of aniline, salicylaldehyde, and potassium cyanide for two to three hours. It can be crystallised from pyridine, has m. p. 258°, and is stable towards acids. Its *acetyl* derivative crystallises from alcohol in pale yellow needles, m. p. 195°, and its *benzoyl* derivative in yellowish-brown prisms, m. p. 227°. J. J. S.

Catalytic Decomposition of Phenylhydrazine by means of Cuprous Halides. ALEXANDER E. ARBUSOFF and W. M. TICHWINSKY (*Ber.*, 1910, **43**, 2295—2296. Compare Struthers, Proc., 1905, **21**, 95).—At 150° phenylhydrazine reacts with cuprous halides according to the equation: $3NHPh\cdot NH_2 + CuCl = 3NH_2Ph + N_2 + NH_3 + CuCl$. The reaction is preceded by the formation of an additive compound, for example, the *compound*, $2NHPh\cdot NH_2,CuI$, has been isolated as colourless prisms, which begin to decompose at 150°.

The rate of decomposition with the different halides has been determined; the reaction proceeds most rapidly with the chloride, and least readily with the iodide. If sufficient care is not taken, the reaction with cuprous chloride may become explosive. J. J. S.

Nitrosophenylhydrazine. EUGEN BAMBERGER and H. HAUSER (*Annalen*, 1910, **375**, 316—333).—The preparation and properties of nitrosophenylhydrazine are described, and also many of its reactions, chiefly in the form of test-tube experiments. It acts as a pronounced reducing agent towards mercuric nitrate, yellow mercuric oxide, silver nitrate, and calcium hypochlorite, being itself oxidised mainly to nitrosobenzene (detected by its odour). Its alcoholic solution, as concentrated as possible, yields at −12° to −15° with a cold saturated alcoholic solution of cupric acetate, *copper nitrosophenylhydrazine*, $Cu(C_6H_6ON_3)_2$, which forms copper-red leaflets with a bronze lustre, is extremely explosive, and inflames in contact with concentrated sulphuric or nitric acid. The solution of the metallic derivative in

acetone gives, almost immediately, a precipitate of copper sulphide with hydrogen sulphide; the reaction, however, is not regarded as ionic, the substance being probably an internally complex salt. When the red copper derivative is treated with acetic acid containing a little water (the absence of water prevents the reaction), nitrogen is evolved and pale grey needles of copper nitrosophenylhydroxylamine are produced. This copper derivative is more conveniently obtained by treating an alcoholic solution of nitrosophenylhydrazine at 0° with a solution (saturated at 5°) of copper acetate in glacial acetic acid (the reaction fails in the presence of 13—15% of water), or by adding nitrosophenylhydrazine to ammoniacal copper hydroxide at −16°. This indirect conversion of nitrosophenylhydrazine into nitrosophenylhydroxylamine is not a case of simple hydrolysis: $NH_2{\cdot}NPh{\cdot}NO + H_2O = OH{\cdot}NPh{\cdot}NO + NH_3$, since it is not appreciably brought about by alkaline reagents, but is probably due to oxidation by the copper oxide: $NH_2{\cdot}NPh{\cdot}NO + O \longrightarrow OH{\cdot}NPh{\cdot}NO + N_2$.

The paper closes with some adverse criticisms of the symmetrical formula, NHPh·NH·NO, suggested by Thiele for nitrosophenyl hydrazine in consequence of its decomposition into aniline and nitrous oxide; in the authors' opinion nitrosophenylhydrazine, like nitrosophenylhydroxylamine (Abstr., 1909, i, 977), is tautomeric:

$$NH_2{\cdot}NPh{\cdot}NO \rightleftharpoons NH{:}NPh{:}N{\cdot}OH \left(\text{or } NH{<}\begin{matrix}NPh\\ |\\ N{\cdot}OH\end{matrix}\right),$$

its compounds with heavy metals being derived from either of the latter formulæ. C. S.

Constitution of Nitrosophenylhydrazine. JOHANNES THIELE and KARL SIEGLITZ (*Annalen*, 1910, **375**, 334—335).—The suggestion advanced by Thiele (Abstr., 1908, i, 927), that nitrosophenylhydrazine has the constitution NHPh·NH·NO has been withdrawn, because benzoylnitrosophenylhydrazine, obtained by the benzoylation of nitrosophenylhydrazine, is converted by stannous chloride and hydrochloric acid into *s*-benzoylphenylhydrazine, from which the benzoylnitrosophenylhydrazine is regenerated by sodium nitrite and acetic acid. C. S.

α-Acylated Phenylhydrazines. OSKAR WIDMANN (*Ber.*, 1910, **43**, 2595).—The author's method of preparing α-acylated phenylhydrazines (Abstr., 1893, i, 411; 1894, i, 57, 512; 1895, i, 31) has been overlooked by Lockemann (this vol., i, 636). C. S.

Influence of the Halogens on Phototropy in Hydrazones. F. GRAZIANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 190—193. Compare this vol., i, 509).—Some hydrazones derived from *p*-bromophenylhydrazine have been prepared to ascertain if the lack of phototropy in certain chloroaniline derivatives (compare Senier and Shepheard, Trans., 1909, **95**, 1943) is due to the presence of the halogen. Of the eight hydrazones examined, four are more or less phototropic, but much less so than the *p*-tolylhydrazones.

Benzaldehyde-*p*-bromophenylhydrazone has m. p. 129° (Biltz and Sieden, Abstr., 1903, i, 120, gave 127·5°), and is phototropic.

Anisaldehyde-*p*-bromophenylhydrazone, m. p. 150° (Ott, Abstr., 1905, i, 376, gave 146—147°), is not phototropic.

Cinnamaldehyde-p-*bromophenylhydrazone*,
$C_6H_4Br\cdot N_2H\colon CH\cdot CH\colon CHPh$,
crystallises in greenish-yellow, lustrous needles, m. p. 143°, and is phototropic.

Cuminaldehyde-p-*bromophenylhydrazone*,
$C_6H_4Br\cdot N_2H\colon CH\cdot C_6H_4\cdot CHMe_2$,
forms yellow, phototropic needles, m. p. 135°.

Piperonaldehyde-p-*bromophenylhydrazone*,
$C_6H_4Br\cdot N_2H\colon CH\cdot C_6H_3\colon O_2\colon CH_2$,
crystallises in colourless laminæ, m. p. 155° (decomp.), and is not phototropic.

p-*Tolualdehyde*-p-*bromophenylhydrazone*, $C_6H_4Br\cdot N_2H\colon CH\cdot C_6H_4Me$, forms small, yellow laminæ, m. p. 162° (decomp.), and is not phototropic.

Vanillin-*p*-bromophenylhydrazone is non-phototropic.

Salicylaldehyde-*p* bromophenylhydrazone has m. p. 171—172° (Biltz and Sieden, *loc. cit.*, gave 175·5°), and is slightly phototropic.

R. V. S.

Relations between Constitution and Phototropy. MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 193—196. Compare this vol., i, 509, and preceding abstract).—The authors have obtained a number of hydrazones derived from 1 : 4 : 5- and 1 : 3 : 5-xylylhydrazines, and have prepared the latter substance for the first time. In agreement with the regularity previously observed, the 1 : 4 : 5-derivatives do not exhibit phototropy. Of the four 1 : 3 : 5-compounds, one is very feebly phototropic.

1 : 4 : 5-Xylylhydrazine hydrochloride has m. p. 209°; Plancher and Caravaggi (Abstr., 1905, i, 158) gave 206°.

Benzaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H\colon CHPh$, forms small, yellow needles, m. p. 89°.

Anisaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4\cdot OMe$, crystallises in small, yellowish-white laminæ, m. p. 117°.

Cinnamaldehyde-1 : 4 : 5-*xylylhydrazone*,
$C_6H_3Me_2\cdot N_2H\colon CH\cdot CH\colon CHPh$,
forms small, yellow needles, m. p. 121°.

Cuminaldehyde-1 : 4 : 5-*xylylhydrazone*,
$C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4\cdot CHMe_2$,
crystallises similarly, and has m. p. 85°.

Piperonaldehyde-1 : 4 : 5-*xylylhydrazone*,
$C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_3\colon O\colon CH_2$,
crystallises in yellow scales, m. p. 135°.

p-*Tolualdehyde*-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4Me$, forms minute, pale yellow scales, m. p. 109°.

Vanillin-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_3(OH)\cdot OMe$, crystallises in very small, colourless needles, m. p. 158°.

Salicylaldehyde-1 : 4 : 5-*xylylhydrazone*, $C_6H_3Me_2\cdot N_2H\colon CH\cdot C_6H_4\cdot OH$, forms pale yellow scales, m. p. 134°.

1 : 3 : 5-*Xylylhydrazine hydrochloride* was prepared by diazotisation

of the corresponding xylidine. It is very soluble in concentrated hydrochloric acid, and was not obtained in pure condition.

Cinnamaldehyde-1 : 3 : 5-*xylylhydrazone* forms yellow crystals, m. p. 142—143° (becoming slightly brown), and is phototropic.

p-*Tolualdehyde*-1 : 3 : 5-*xylylhydrazone* crystallises in rosettes of yellow needles, m. p. 119°, and is not phototropic.

Piperonaldehyde-1 : 3 : 5-*xylylhydrazone* forms yellow, non-phototropic needles, m. p. 135—136° (yielding a brown liquid).

Anisaldehyde-1 : 3 : 5-*xylylhydrazone* crystallises in small, yellow needles, m. p. 144—145° (giving a brown liquid). R. V. S.

Preparation and Phototropy of Some Osazones. MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 302—307. Compare Padoa and Graziani, this vol., i, 509).—Continuing the study of phototropy, the authors have prepared osazones from benzil and piperil with *o*- and *p*-tolyl- and β-naphthyl-hydrazines. Even on combining these results with those of Biltz (Abstr., 1900, ii, 125), no connexion between constitution and phototropy becomes evident. Of the two isomeric forms to be expected, only the β-modification was obtained in every case.

β-*Benzil*-p-*tolylosazone*, $C_2Ph_2(:N\cdot NH\cdot C_6H_4Me)_2$, obtained by Pickel's method (Abstr., 1886, 545), is a yellow, crystalline, phototropic substance, m. p. 152°.

β-*Piperil*-p-*tolylosazone*, $\begin{matrix} CH_2:O_2:C_6H_3\cdot C:N\cdot NH\cdot C_6H_4Me \\ CH_2:O_2:C_6H_3\cdot C:N\cdot NH\cdot C_6H_4Me \end{matrix}$, similarly prepared, crystallises in small, sulphur-yellow needles, m. p. 215°, and is phototropic.

β-*Benzil*-β-*naphthylosazone*, $C_2Ph_2(:N\cdot NH\cdot C_{10}H_7)_2$, obtained by the same method, forms yellow needles, m. p. 211·5°. It is phototropic, and one specimen of it showed phototropic change in either direction with remarkable rapidity, possibly owing to the presence of some impurity catalytically affecting the process.

β-*Piperil*-β-*naphthylosazone*, similarly prepared, is a yellow, crystalline, phototropic substance, m. p. 207°.

β-*Benzil*-o-*tolylosazone* was prepared by Purgotti's method (*Gazzetta*, 1892, 14, ii, 611), and forms a canary-yellow, crystalline, phototropic powder, m. p. 170°.

β-*Piperil*-o-*tolylosazone*, obtained by the same method, is a yellow, crystalline powder, m. p. 206·5°, and is phototropic. It becomes bright red instantly in sunlight, and may be said to be the most sensitive phototropic substance yet prepared. R. V. S.

Rearrangement in the Quinone Group. ERNST BÖRNSTEIN (*Ber.*, 1910, 43, 2380—2384).—The base obtained by the action of sulphuric acid on *p*-toluidino-*p*-toluquinonetolylimide (Abstr., 1901, i, 376) has the same composition as the original compound, and is regarded as 7-p-*toluidino*-3 : 6-*dimethylphenoxazine*,

$$C_7H_7\cdot NH\cdot C_6H_2Me{<}{\substack{O \\ NH}}{>}C_6H_3Me.$$

It crystallises from ethyl alcohol or dilute acetone in brownish, orange-yellow needles or plates, m. p. 173°. The *hydrochloride*, $C_{21}H_{20}ON_2,HCl$,

forms red rhombohedra, with a greenish, metallic reflex. The *platinichloride*, $2C_{21}H_{20}ON_2,H_2PtCl_6$, has a yellowish-red colour. The *sulphate*, $C_{21}H_{20}ON_2,H_2SO_4$, crystallises from alcohol in deep, red compact cubes. The *picrate*, $C_{27}H_{23}O_8N_5$, forms golden-yellow, microscopic needles, m. p. 227°. The base yields a phenylcarbimide *derivative*,

$$C_{21}H_{20}ON_2,C_7H_5ON,$$

as colourless rosettes of needles, m. p. 188° (decomp.).

Attempts to acetylate, methylate, and form an oxime gave negative results. When reduced, the base yields *p*-toluidine. J. J. S.

Preparation of 5 : 5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 225457).—The action of oxalyl chloride on dialkylmalonamides affords 78—80% of the theoretical yield of the respective dialkylbarbituric acid.

Equal weights are heated together on the water-bath during several hours, water is added, and the product collected. F. M. G. M.

Condensation Products of Alloxan. OTTO KÜHLING (*Ber.*, 1910, 43, 2406—2417. Compare Abstr., 1905, i, 944; 1908, i, 571; Kühling and Schneider, *ibid.*, 1909, i, 424).—Alloxan condenses with ethyl benzoylacetate or the corresponding methyl ester in the presence of a mixture of water and alcohol, saturated at − 6° to − 8°, with hydrogen chloride, yielding carbethoxy- or carbomethoxy-phenacyldialuric acid. These compounds resemble the phenacyldialuric acids as regards their behaviour towards dilute acids or acetic anhydride, but are readily decomposed into their components when boiled with water, mixed with sodium carbonate solution at the ordinary temperature, or treated with the usual reagents for ketones. The acetyl derivatives, are more stable, and react with sodium carbonate solution, yielding compounds which are regarded as carbethoxy(methoxy)-phenacylbarbituric acids.

Carbethoxyphenacyldialuric acid,

$$CO_2Et\cdot CHBz\cdot C(OH)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

crystallises from alcohol in rhombic prisms, m. p. 207—208° (decomp.) after turning red at 180°. When boiled for several hours with 12% hydrochloric acid, it yields phenacyldialuric acid. The *acetyl* derivative, $CO_2Et\cdot CHBz\cdot C(OAc)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$, crystallises in long plates, melts at 167—168°, then solidifies, and melts again at 235—236°. *Carbethoxyphenacylbarbituric acid*, $CO_2Et\cdot CHBz\cdot CH<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$, crystallises from alcohol in prisms, m. p. 239—240°, and is also formed when the acetyl derivative is heated at 180—190°. It yields a *sodium* salt, $C_{15}H_{13}O_6N_2Na$, in the form of prismatic needles, and reacts with benzenediazonium chloride solution, yielding alloxanphenylhydrazone. With phenylhydrazine in acetic acid solution, the barbituric acid yields a yellow, amorphous precipitate, and yellowish-red crystals of a *compound*, $C_{21}H_{18}ON_4$, m. p. 174—175°, which is probably a *keto-anilinodiphenyltetrahydrotriazine*, $CPh<\begin{matrix}CH_2\text{——}CO\\N\cdot NPh\cdot N\cdot NHPh\end{matrix}$.

Carbomethoxyphenacyldialuric acid,

$$CO_2Me\cdot CHBz\cdot C(OH)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

forms colourless prisms, m. p. 221° (decomp.). The *acetyl* derivative, $C_{16}H_{14}O_8N_2$, also forms prisms, melts at 158°, resolidifies, and again melts at 241—242°. *Carbomethoxyphenacylbarbituric acid*, $C_{14}H_{12}O_6N_2$, forms colourless needles, m. p. 246—247° (decomp.). J. J. S.

Compounds of Piperazine with Phenols. H. Stévignon (*Bull. Soc. chim.*, 1910, [iv], 7, 922—926).—Schmidt and Wichmann have shown that piperazine forms additive compounds with phenol and with quinol (Abstr., 1892, 210), and the author has extended this observation to other phenols, and finds that 1 mol. of piperazine combines with 2 mols. of a monohydric phenol or with 1 mol. of a dihydric phenol. In all cases the two substances were allowed to react in alcohol.

The following substances were prepared: *Di-*o*-cresolpiperazine*, m. p. 51—52° (approx.), pale yellow crystals. *Dicarvacrolpiperazine*, m. p. 85—86° (approx.), colourless needles. *Dithymolpiperazine*, m. p. 88°, brilliant, colourless needles. *Di-β-naphtholpiperazine*, m. p. 110° (approx.), greyish-white crystals. *Catecholpiperazine*, bright brown needles. *Diguaiacolpiperazine*, m. p. 98° (approx.), brilliant colourless lamellæ. The piperazine in these compounds behaves as a diacidic base, and can be titrated directly with *N*/10-sulphuric acid, using helianthin-*A* as indicator. T. A. H.

Action of Sulphuric and Hydrochloric Acids on *endo*Bisazo-derivatives. I. Henri Duval (*Bull. Soc. chim.*, 1910, [iv], 7, 915—922).—It is shown that under the action of sulphuric or hydrochloric acid, the *endo*bisazo-compounds behave like azodiazo-compounds, one azo-group being replaced by a hydroxyl group, which in the case of hydrochloric acid is then replaced by chlorine, whilst the second remains intact. Instances of this reaction have been given already (Abstr., 1907, i, 663), and are now repeated with experimental details. The author suggests that the substances now called indazoles should be re-named *iso*azindoles, and that the present *iso*azindoles should be named azindoles.

When 4 : 4′-diacetylbisazodiphenylmethane [4 : 6′-diacetylphenylbenz*iso*indazole] (Abstr., 1908, i, 706) is heated with a 53% solution of sulphuric acid at 100—105°, it is converted in the course of a few minutes into 2′-hydroxy-4 : 6′-diacetyl-3-phenylbenz*iso*indazole,

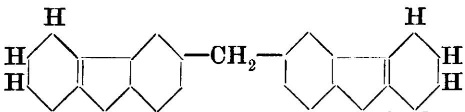
$$HO\cdot C_6H_3Ac\cdot CH<\begin{matrix}\text{———}N\\C_6H_3Ac\end{matrix}>N,$$

which in the author's new nomenclature would be "2′-hydroxy-4′ : 6-diacetyl-3-phenylindazole." It melts at 235°, forms bright yellow needles from alcohol, and is soluble in dilute sodium hydroxide solution, but not in ammonia. T. A. H.

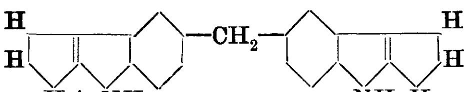
Quinoline and Indole Derivatives from *para*Diaminodiphenylmethane. Walther Borsche and G. A. Kienitz (*Ber.*, 1910, 43, 2333—2337).—6 : 6′-*Diquinolylmethane*, $CH_2(C_9NH_6)_2$, can be prepared from *p*-diaminodiphenylmethane by the usual Skraup synthesis. It

forms a limpid, brown oil, which solidifies slowly, and can be obtained as colourless needles, m. p. 160°.

4:4'-*Dihydrazinodiphenylmethane*, $CH_2(C_6H_4{\cdot}NH{\cdot}NH_2)_2$, prepared by diazotising β-diaminodiphenylmethane and reducing the diazo-compound by Fischer's method, crystallises from benzene in colourless plates, m. p. 71—72°, but turns brown in the course of a few hours when exposed to the air. The *hydrochloride* forms a white, crystalline powder, and is somewhat more stable. The *dibenzylidene* derivative, $CH_2(C_6H_4{\cdot}NH{\cdot}N{:}CHPh)_2$, crystallises from glacial acetic acid in golden-yellow plates, m. p. 193—194°. The condensation product with dextrose, $CH_2(C_6H_4{\cdot}NH{\cdot}N{:}CH{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH)_2$, is a dark yellow, crystalline powder, m. p. 122—123° (decomp.).



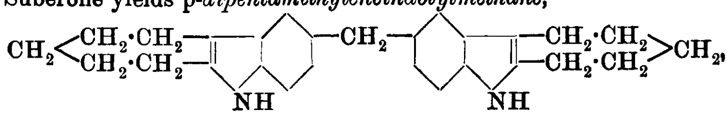
(I.)



(II.)

The condensation product with *cyclo*hexanone readily loses ammonia when warmed with glacial acetic acid (Abstr., 1908, i, 365), and yields p-*di-αβ-tetramethyleneindolylmethane* (*bistetrahydrocarbazolylmethane*, formula I.), which separates from dilute acetone in yellow crystals, m. p. 265°. From *cyclo*pentanone, p-*di-αβ-trimethyleneindolylmethane* (formula II) is formed in a similar manner; it separates from dilute acetic acid in a yellow powder, m. p. 262°.

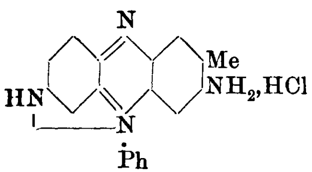
Suberone yields p-*dipentamethyleneindolylmethane*,



which does not melt at 300°. J. J. S.

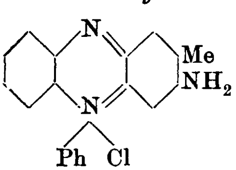
Synthesis of the Safranines. W. G. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 505—512. Compare Barbier and Sisley, Abstr., 1905, i, 840).—The author disagrees with the ordinarily accepted view of the formation of the safranines and indulines, namely, that the first products of the reaction are indamines which then condense with the amines. *p*-Benzoquinonedi-imide is quite inert towards amines, only reacting when one of the hydrogen atoms of the amino-group is displaced by a halogen, and this the more readily the greater the atomic weight of the halogen. It is, therefore, probable that the first product in the formation of the safranines is *p*-benzoquinonedichlorodi-imide (or a similar compound), which then reacts with the amines. The tertiary amines only form these condensation products when they have the property of readily losing one of their radicles. The secondary and primary amines are equally active, although some primary amines, such as tribromoaniline and dibromotoluidine, do not react at all or with difficulty. In all cases an excess of the amine is favourable to a good yield, and as the molecular weight of the amine increases, the number of molecules

of the amine that combine with one of the *p*-benzoquinonedichlorodi-imide decreses. Polyamines, particularly *m*-diamines, react readily with *p*-benzoquinonedichlorodi-imide. If in a mixed secondary and primary amine, a methyl group is introduced in an ortho-position to the primary amino-group, the compound so formed reacts very readily with *p*-benzoquinonedichlorodi-imide. Thus 4-phenyltolylene-2 : 4-diamine reacts readily with the quinone, forming the leuco-compound of indamine, which passes readily into indamine and then by loss of the heavier amino-group can be converted into the azone (annexed formula), which is the formula proposed for safranine. Its advantages over the formula hitherto accepted are discussed. Thus it readily explains why only one amino-group reacts when safranine is diazotised ; also, why only a monoacetyl derivative is obtained and so forth. This method of obtaining safranines is claimed to be far better than any method hitherto described. Z. K.



Synthesis of the Simplest Safranine: 3:6-Diamino 5-phenazonium Chloride. W. G. SAPOSHNIKOFF and N. N. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 512—522. Compare preceding abstract).—3 : 6-*Diamino-5-phenyl-2-methylphenazonium chloride* was prepared by heating a mixture of *p*-benzoquinonedichlorodi-imide (1 mol.) and 4-phenyltolylene-2 : 4-diamine (2 mols.) in alcoholic solution on a water-bath for fifteen to twenty minutes. The yield is 86·7—93·2% of the theoretical. The substance forms bright yellow crystals soluble in concentrated sulphuric acid with an emerald-green colour, turning violet and red on dilution. The base is precipitated by alkali hydroxides, but not by alkali carbonates, and is readily soluble in water. The *nitrate* and *chromate*, $(C_{19}H_{17}N_4)_2Cr_2O_7$, were prepared.

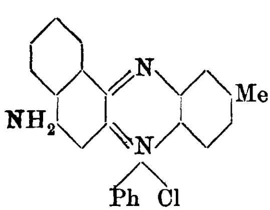
The *diacetyl* derivative, $C_{23}H_{21}O_2N_4Cl$, crystallises from alcohol in yellowish-green, and from glacial acetic acid in brick-red, crystals, of which the chromate was prepared. By eliminating one amino-group by means of the diazo-reaction, monomethyl*apo*safranine (annexed formula) is obtained (compare Kehrmann and Wetter, Abstr., 1898, i, 437). It forms a *chromate*, $(C_{19}H_{16}N_3)_2Cr_2O_7$.



By removing the amino-group from methyl*apo*safranine, or both amino-groups from the original safranine, phenotoluophenazonium is formed. Diazosafranine condenses with β-naphthol to form a blue *dye*, of which the *chromate*, $(C_{29}H_{22}O_2N_5)_2Cr_2O_7$, was analysed. Z K.

Synthesis of Safranine with a Naphthalene Nucleus (3:6-Diamino-5-phenyl-2-methylnaphthaphenazonium Chloride). N. N. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 522—530. Compare preceding abstract).—3 : 6 - *Diamino* - 5-*phenyl* - 2 - *methylnaphthaphenazonium chloride*, prepared from naphthaquinonedichlorodi-imide and 4-phenyltolylene-2 : 4-diamine, forms yellowish-green crystals; the *chromate*, $(C_{23}H_{19}N_4)_2Cr_2O_7$, is described. By eliminating one amino-

group, the *monoamino*-compound (annexed formula) is obtained, of which



the *chromate*, $(C_{23}H_{18}N_3)_2Cr_2O_7$, was analysed; the *acetyl* derivative forms green crystals. On removing the amino-group, the chromogen, *5-phenyl-2-methylnaphthaphenazonium*, isolated as the *ferrichloride*, $C_{23}H_{17}N_2Cl_4Fe$, m. p. 205°, is obtained. The latter is converted, in ammoniacal solution, into the amino-compound. The diazotised naphthasafranine gives a blue *dye* with β-naphthol, the *chromate*, $(C_{33}H_{24}ON_5)_2Cr_2O_7$, of which was analysed. Z. K.

Furoxans. IV. Action of Amines on Dibenzoylfuroxan. HEINRICH WIELAND and ERWIN GMELIN (*Annalen*, 1910, **375**, 297—307. Compare Abstr., 1901, i, 609, 610).—The authors' recent work (*loc. cit.*) has shown that the furoxan ring is very easily ruptured by ammonia or amines, amidoximes being produced, thus:

$$\begin{array}{l}\cdot C\text{—}CH \\ \;\,\| \quad\;\; | \\ N\cdot O\cdot N\end{array}\!\!>\!O \xrightarrow{RN\cdot H_2} \begin{array}{l}\cdot C\text{———}C\cdot NHR \\ \;\,\| \qquad\quad\; \| \\ NOH \quad N\cdot OH\end{array}.$$

Under suitable conditions the amidoxime may experience ring closure, with the production of *iso*oxazole derivatives. These results are utilised to show that Boeseken's benzoyl-*p*-bromoanilinofurazan (this vol., i, 643), obtained by warming diphenyldinitrosacyl (dibenzoylfuroxan) with ethereal *p*-bromoaniline, is not a furazan, but a nitroso*iso*oxazole derivative. Using ethereal aniline (2 mols.), the authors obtain, after the removal of the precipitated benzanilide and evaporation of the solvent, an orange-coloured syrup of the unstable anilino-oxime, OH·N:CBz·C(:N·OH)·NHPh, which is converted by warm acetic acid into *4-nitroso-3-anilino-5-phenyl*iso*oxazole*,

$$\begin{array}{l}CPh:C(NO) \\ | \\ O\text{————}N\end{array}\!\!>\!C\cdot NHPh\,;$$

this crystallises in brownish-red needles, and is reduced in alcoholic solution by zinc dust and acetic acid to *4-amino-3-anilino-5-phenyl*iso*oxazole*, m. p. 147° (decomp.). An acetic acid solution of the latter is converted by sodium nitrite at 0° into an unstable, red nitrosoamine, $\begin{array}{l}CPh:C(NH_2) \\ | \\ O\text{————}N\end{array}\!\!>\!C\cdot NPh\cdot NO$, which rapidly changes to *diphenyl-3:4-gem-triazolo*iso*oxazole* (*3:4-phenylazimino-5-phenyl*iso*oxazole*),

$$O\!<\!\begin{array}{l}CPh:C\text{—}N \\ \qquad\quad | \\ N=C\cdot NPh\end{array}\!\!>\!N,$$

m. p. 151° (decomp.), which crystallises in yellow leaflets, gives a magenta coloration with phenol and sulphuric acid, and develops a dark green coloration with sulphuric acid alone.

When warmed with alcohol or acetic acid, the brownish-red nitroso-anilinophenyl*iso*oxazole is converted into the isomeric, colourless azoxime, 3-benzoyl-5-anilino-1:2:4-oxadiazole, $\begin{array}{l}CBz\cdot N \\ \| \\ N\text{——}O\end{array}\!\!>\!C\cdot NHPh$ (as stated by Böeseken), the formation of which is explained by the intermediate production of the furazan ring, $\begin{array}{l}CBz=\!=\!=N \\ | \\ C(NHPh):N\end{array}\!\!>\!O$,

which then undergoes a partial Beckmann transformation (Böeseken, *loc. cit.*).

[With ALEX. ROSEEU.]—Results similar to the preceding are obtained when dibenzoylfuroxan is decomposed by *p*-anisidine. 4-*Nitroso*-3-p-*anisidino*-5-*phenyl*iso*oxazole*, decomp. 123°, crystallises in glistening, black needles, forms dark red solutions, is converted by boiling alcohol mainly into the isomeric azoxime, and is reduced by zinc and acetic acid to 4-*amino*-3-p-*anisidino*-5-*phenyl*iso*oxazole*, m. p. 151°. This base in acetic acid is converted by sodium nitrite into *phenyl*-p-*anisyl*-3 : 4-gem-*triazolo*iso*oxazole*,

$$O{<}\begin{matrix}CPh{:}C\text{———————}N\\ \quad\;\;|\\ N{=\!=}C{\cdot}N(C_6H_4{\cdot}OMe)\end{matrix}{>}N,$$

decomp. 141°, which crystallises in golden-yellow leaflets.

Contrary to Böeseken's statement that dibenzoylfuroxan only reacts with primary amines, the authors find that a vigorous reaction occurs with ethereal piperidine. C. S.

Urazoles. XVII. Rearrangement of the Tautomeric Salts of 1 : 4-Diphenyl-5-thionurazole and 1 : 4-Diphenyl-5-thiolurazole. SIDNEY NIRDLINGER and SALOMON F. ACREE (*Amer. Chem. J.*, 1910, **44**, 219—251).—The slow rearrangement of tautomeric acids and their final states of equilibrium have been investigated by several authors, but the tautomeric salts of such acids have not hitherto been studied. In view of the importance of such work as a test of the validity of Acree's theory, an investigation has now been made of the salts of 1 : 4-diphenyl-5-thionurazole and 1 : 4-diphenyl-5-thiolurazole.

It has been shown by Busch and Holzmann (Abstr., 1901, i, 234) that Marckwald's thiosemicarbazides (Abstr., 1893, i, 46) are structural isomerides of the types $NH_2{\cdot}NR{\cdot}CS{\cdot}NHR$ and $NHR{\cdot}NH{\cdot}CS{\cdot}NHR$.
By the action of carbonyl chloride on $\beta\delta$-diphenylthiosemicarbazide, a compound, m. p. 141°, is obtained, which was regarded by Busch and Holzmann (*loc. cit.*) as 5-thiol-1 : 4-diphenylurazole,

$$NPh{<}\begin{matrix}C(SH){\cdot}NPh\\ {>}O\quad\;|\\ C{=\!=\!=}N\end{matrix}$$

Busch (Abstr., 1902, i, 322) has stated that when this substance is heated, it undergoes transformation into a compound, m. p. 219—221°, which he assumed to be 5-thion-1 : 4-diphenylurazole, $NPh{<}\begin{matrix}CS{-}NPh\\ CO{\cdot}NH\end{matrix}$ or $NPh{<}\begin{matrix}CS\text{——}NPh\\ C(OH){:}N\end{matrix}$, or a mixture of the two forms in equilibrium. It is now shown, however, that these views are incorrect, and that the compound of m. p. 141° is actually 5-thion-1 : 4-diphenylurazole, capable of existing in two forms in equilibrium, whilst the compound of m. p. 219—221° is 5-thiol-1 : 4-diphenylurazole.

By the action of diazomethane and diazoethane on 5-thion-1 : 4-diphenylurazole and 5-thiol-1 : 4-diphenylurazole, compounds are obtained which differ from those produced by the action of alkyl iodides

on the sodium salts of the urazoles. With diazomethane, 5-thion-1 : 4-diphenylurazole yields a *compound*, $C_{15}H_{13}ON_3S$, m. p. 74·5—75·5°, and with diazoethane it furnishes an *ester*, $C_{16}H_{15}ON_3S$, m. p. 79—81°. By the action of diazomethane on 5-thiol-1 : 4-diphenylurazole, an *ester*, m. p. 129·5—130·5°, is produced, isomeric with that obtained from the thionurazole. The thiolurazole and diazoethane give an *ester*, m. p. 105·5—107·5°.

It has been found that 5-thion-1 : 4-diphenylurazole and 5-thiol-1 : 4-diphenylurazole yield sodium salts which are reconverted into the respective urazoles on addition of hydrochloric acid. Both salts react with methyl iodide, and the reaction takes place about eighty times as rapidly with the salt of the thiolurazole as with that of the thionurazole. The *methyl* ester of the thionurazole is obtained as a red, viscous oil, which gradually becomes semi-solid. The methyl ester of the thiol compound is identical with that obtained by the action of carbonyl chloride on $\beta\delta$-diphenyl-γ-methylthiosemicarbazide.

The sodium salts have been esterified quantitatively, and a method has been devised for analysing mixtures of the salts or esters depending on the fact that, under certain conditions, the methyl ester of 5-thiol-1 : 4-diphenylurazole is completely hydrolysed by alkali hydroxide in presence of chloroform, whilst that of the thionurazole is but little affected by this treatment.

The sodium salts of the two urazoles are mutually convertible into one another by two apparently reversible unimolecular reactions, the velocity of rearrangement of sodium 5-thion-1 : 4-diphenylurazole being about nine times as great as that of sodium 5-thiol-1 : 4-diphenylurazole. E. G.

5-Hydroxy-1 : 2 : 3-triazole. THEODOR CURTIUS and AUGUST BOCKMÜHL (*Ber.*, 1910, 43, 2441—2446).—5-Hydroxy-1 : 2 : 3-triazole,

$$\begin{array}{l} N{=\!=\!=\!=}N \\ | \\ CH{:}C(OH) \end{array}\!\!>\!NH,$$

was prepared by Curtius and Thompson (Abstr., 1907, i, 95) from diazoacetamide, and by Dimroth and Aickelin (Abstr., 1907, i, 159) from ethyl-1-phenyl-5-triazolonecarboxylate. It has now been more closely studied (compare Dimroth, this vol., i, 518). 5-Hydroxytriazole has m. p. 129°; it is a monobasic acid, and forms a colourless, crystalline *potassium* salt and a *hydrazonium* salt, $C_2H_2N_3(ON_2H_5)$, crystallising in needles, m. p. 117°. An ammonium salt could not be prepared; on evaporation to dryness with ammonia, a colourless, crystalline substance was obtained of the same composition as hydroxytriazole, m. p. about 95°. On the addition of bromine water to an aqueous solution of 5-hydroxytriazole, it decomposes, the gas evolved consisting of molecular proportions of nitrogen and carbon monoxide. Probably dibromoglycollic acid (Curtius and Welde, Abstr., 1907, i, 449) is first formed, and decomposes into oxalic acid, which yields carbon monoxide. E. F. A.

Diazoacetylglycinehydrazide and 5-Hydroxy-1 : 2 : 3-triazole 1-acetylhydrazide. THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1910, 43, 862—880).—Curtius and Thompson (Abstr., 1906, i, 404, 940;

1907, i, 95) have shown that ethyl diazoacetylglycine yields derivatives of 5-triazolone-1-acetic acid when treated with ammonia or alkali, and the present authors find that hydrazine hydrate reacts similarly with the ester.

Diazoacetylglycinehydrazide, $N_2:CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, prepared by boiling hydrazine hydrate with ethyl diazoacetylglycine (for which an improved method of preparation is given) in alcoholic solution, crystallises in yellow, glistening leaflets, which darken at 120° and decompose at 147°; the *benzylidene* derivative,

$$N_2:CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N:CHPh,$$

forms minute, almost colourless needles, m. p. 199—200°, and the iso*propylidene* derivative, $N_2:CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N:CMe_2$, crystallises in bright yellow, glistening leaflets, m. p. 178° (decomp.). When treated with hydrogen chloride in alcoholic solution, the diazohydrazide yields *chloroacetylglycinehydrazide hydrochloride*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,HCl,$$

a colourless powder, m. p. 168°; the *benzylidene* derivative of the base is a colourless powder, which does not melt at 300°.

When a cold aqueous solution of diazoacetylglycinehydrazide is treated with a trace of sulphuric acid, nitrogen is evolved, and the solution with benzaldehyde furnishes *hydroxyacetylglycinebenzylidenehydrazide*, $OH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N:CHPh$, crystallising in small, colourless needles, m. p. 143°.

Hydrazonium 5-*hydroxy*-1 : 2 : 3-*triazole*-1-*acetylhydrazide*,

$$\begin{matrix} CH\cdot N{=}N \\ \| \\ C(ON_2H_5) \end{matrix}\!\!>\!N\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is formed as a by-product in the preparation of diazoacetylglycinehydrazide, and is obtained in larger yield by heating ethyl diazoacetylglycine in more concentrated solution with a greater excess of hydrazine hydrate; it forms pale red, feathery crystals, m. p. 175° (decomp.). The *potassium* (m. p. 245°, decomp.) and *silver* (decomp. 200°) salts are described. The *hydrazonium* salt of 5-hydroxytriazole-1-acetic acid, $C_2HN_3(ON_2H_5)\cdot CH_2\cdot CO_2\cdot N_2H_5$ (reddish needles, m. p. 172°), was also prepared.

5-*Hydroxy*-1 : 2 : 3-*triazole*-1-*acetylhydrazide*, $C_4H_7O_2N_5,H_2O$, prepared from the potassium or silver salt, crystallises in colourless, right-angled tablets, m. p. 147°, which are anisotropic; the *hydrochloride*, a colourless powder, m. p. 174° (decomp.), the *benzylidene* derivative,

$$C_2HN_3(OH)\cdot CH_2\cdot CO\cdot NH\cdot N:CHPh,$$

m. p. 190° (decomp.), and the iso*propylidene* derivative, m. p. 155—160°, were prepared. J. C. C.

Diazoacetylglycylglycinehydrazide. THEODOR CURTIUS and THOMAS CALLAN (*Ber.*, 1910, **43**, 2447—2457).—Curtius and Welde (preceding abstract) have shown that ethyldiazoacetylglycine and hydrazine hydrate yield at first diazoacetylglycinehydrazide, which with a further amount of hydrazine hydrate undergoes rearrangement to the *hydrazonium* salt of 5-hydroxytriazole-1-acetylhydrazide. It is now shown that ethyldiazoacetylglycylglycine forms *diazoacetylglycylglycinehydrazide*. This has the properties of a true diazo-compound and also of an acid hydrazide, liberates nitrogen with dilute mineral

acids, and forms a crystalline compound with benzaldehyde. When boiled in aqueous solution, *hydroxyacetylglycylglycinehydrazide*,

$$OH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is formed. Prolonged boiling of the hydrazide with hydrazine hydrate converts it into a yellow oil, the *hydrazonium* salt of 5-*hydroxytriazole*-1-*acetylglycinehydrazide*, the *benzylidene* derivative of which was obtained crystalline. The triazole derivative is more readily obtained on warming the hydrazide with dilute alcoholic potassium hydroxide, when the *potassium* salt is obtained as a colourless, very hygroscopic substance. The benzylidene derivative of the triazole, as also that of the 5-hydroxytriazole-1-acethydrazide of Curtius and Welde (*loc. cit.*), combines with *p*-toluenediazonium sulphate, forming red- and orange-hued azo-dyes respectively.

Diazoacetylglycylglycinehydrazide,

$$N_2{:}CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

crystallises in lustrous, yellow needles, aggregated in rosettes, m. p. 167° (decomp.). *Diazoacetylglycylglycinebenzylidenehydrazide* is a yellow, amorphous powder, m. p. 180—181° (decomp.).

Hydroxyacetylglycylglycinehydrazide is a colourless, very soluble powder, which blackens at 230°, decomp. 240°. *Hydroxyacetylglycylglycinebenzylidenehydrazide* forms short, colourless plates, decomp. 240°.

Acetylhydroxyacetylglycylglycinehydrazide,

$$OAc\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is a colourless, microcrystalline powder, decomp. 180°.

5-*Hydroxytriazole*-1-*acetylglycinehydrazide*,

$$\left.\begin{array}{l} N{=\!=\!=}N \\ | \\ CH{:}C(OH) \end{array}\right\rangle N\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2\,;$$

the *hydrazonium* salt is a colourless oil, soluble in water with a strongly alkaline reaction; the *potassium* salt is a colourless, crystalline mass.

5-*Hydroxytriazole*-1-*acetylglycinebenzylidenehydrazide* is a pale brown, amorphous powder, m. p. 180° (decomp.). It condenses with *p*-toluenediazonium sulphate in dilute sodium hydroxide solution, forming 4-*tolueneazo*-5-*hydroxytriazole*-1-*acetylglycinebenzylidenehydrazide*, which crystallises in small, reddish-brown needles, m. p. 151·5°.

4-*Tolueneazo*-5-*hydroxytriazole*-1-*acetylbenzylidenehydrazide* forms an orange powder, m. p. 149·5° (decomp.). E. F. A.

Transformation of Diazo-hydrazides into Monohalogen Hydrazides and Azoimides. THEODOR CURTIUS and THOMAS CALLAN (*Ber.*, 1910, **43**, 2457—2467).—By the action of gaseous hydrogen chloride on diazoacetylglycinehydrazide, Curtius and Welde (this vol., i, 786) obtained chloroacetylglycinehydrazide hydrochloride. The action of hydrogen bromide and hydrogen iodide has now been studied in a similar manner. The iodine derivative could not be obtained pure, but it condenses with benzaldehyde to form *iodoacetylglycinebenzylidenehydrazide*, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh$. Two other compounds are also formed together with the iodo-derivative, the one, formed in small quantity only, has a high melting point, and is probably the symmetrical secondary hydrazide of iodoacetylglycine. The other, $C_6H_{12}O_2N_3I$, crystallises from alcohol in needles; when boiled

with water an ethyl group disappears, and it is supposed that the original compound contains an ethyl group in the hydrazine residue.

When treated with a concentrated aqueous solution of sodium nitrite, the halogen acetylglycinehydrazides are converted into halogen acetylglycineazoimides. These melt and decompose explosively at higher temperatures; they form anilides with aniline, and boiling with alcohol converts them into urethanes.

By the action of hydrogen chloride on diazoacetylglycylglycinehydrazide, a colourless powder, m. p. 172—174°, was obtained, which did not correspond in composition with chloroacetylglycylglycinehydrazide hydrochloride.

Chloroacetylglycineazoimide, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_3$, crystallises from ether in well-formed, colourless, lustrous plates. The aqueous solution when heated desposits a colourless, insoluble powder, m. p. 184—185°.

Chloroacetylglycineanilide forms centimetre-long, colourless needles, m. p. 170—171°.

Chloroacetylaminomethylurethane, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$, crystallises in beautiful plates of silky lustre, m. p. 149—150°.

Bromoacetylglycinehydrazide hydrobromide, prepared by the action of hydrogen bromide on diazoacetylglycinehydrazide in alcoholic solution, is a heavy, crystalline powder, deliquescent in the air, decomp. 115°.

Bromoacetylglycinebenzylidenehydrazide is a colourless, amorphous powder, m. p. 187—190° (decomp.).

Bromoacetylglycineazoimide crystallises from ether in colourless, silky, lustrous plates. It melts and explodes when heated on a spatula.

Bromoacetylglycineanilide crystallises in bunches of intergrown, small needles, m. p. 161—162°.

Bromoacetylaminomethylurethane separates from alcohol in colourless plates, m. p. 154—155°.

Iodoacetylglycinebenzylidenehydrazide was obtained as an almost colourless, amorphous powder, m. p. 177—179°.

Iodoacetylglycineazoimide forms colourless platelets, which melt and explode.

Iodoacetylaminomethylurethane crystallises in well-formed, colourless plates, m. p. 171° (decomp.).

Iodoacetylglycine-ethylhydrazide (?) was obtained in colourless, microscopic needles, m. p. 147—148°. When boiled with water a *residue*, m. p. 102—104° (decomp.), remained, which with benzaldehyde formed the above-described iodoacetylglycinebenzylidenehydrazide.

Iodoacetylglycineamide, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of hydrogen iodide on diazoacetylglycineamide, crystallises in glistening, colourless needles and plates, m. p. 173—175°.

E. F. A.

Hydrazidicarboxylhydrazide. Robert Stollé [and, in part, K. O. H. Leverkus and R. Krauch] (*Ber.*, 1910, **43**, 2468—2470 Compare Curtius and Heidenreich, Abstr., 1895, i, 12; 1896, i, 143).—On prolonged boiling of ethyl hydrazidicarboxylate with hydrazine

hydrate in alcoholic solution, the hydrazine salt of hydrazidicarboxylamide separates out. The mother liquors, when shaken with benzaldehyde, yield *dibenzylidenehydrazidicarboxylhydrazide*,

$$CHPh:N\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot N:CHPh,$$

crystallising $+H_2O$ in slender plates, m. p. 229°.

Hydrazidicarboxylhydrazide hydrochloride, prepared from the benzylidene compound by heating with hot hydrochloric acid, crystallises in small, glistening prisms, decomp. 203°. The *condensation product* with anisaldehyde has m. p. 218°, that with salicylaldehyde has m. p. 238°. On heating ethylhydrazidicarboxylate with hydrazine hydrate at 70° and evaporating to dryness in a vacuum, *hydrazidicarboxylhydrazide*, $NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2$, is obtained in monoclinic prisms, m. p. 196°. It reduces ammoniacal silver nitrate in the cold, and Fehling's solution when warmed. The *sulphate* ($+H_2O$) crystallises in strongly refractive prisms, m. p. 210° (decomp.).

Hydrazidicarboxylazoimide has m. p. 146°, and detonates very violently. With aniline in ethereal solution it forms *hydrazidicarboxylanilide.*

Hydrazidicarboxylethylamide crystallises in plates, m. p. 255°. *Hydrazidicarboxylphenylhydrazide* has m. p. 213° (decomp.).

E. F. A.

Stereomeric Azobenzenes. CATHERINE V. GORTNER and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1910, **32**, 1294—1296).—Although it is evident from the structural formula of azobenzene that it should be capable of existence in *syn*- and *anti*-modifications, only one form has hitherto been described.

On heating azoxybenzene with iron filings, a distillate was obtained which consisted of a red liquid containing a crystalline substance. On removing the red liquid by means of light petroleum, in which it is readily soluble, a *substance*, m. p. 237° (corr.), was left in the form of light grey needles, representing about 1% of the azoxybenzene used. This substance was not further investigated.

The deep red solution was washed with cold dilute hydrochloric acid and afterwards with water, and was filtered and left to evaporate. In several cases, only ordinary azobenzene, m. p. 68°, crystallising in prisms, was obtained, but, in other cases, a deep red liquid was left, which furnished a stereoisomeride, m. p. 25° (corr.), crystallising in stellate groups of needles. From a mixture of the two isomerides, that melting at 68° may be removed by crystallisation, the new form being left in the mother liquor. The latter modification is probably *syn*-azobenzene. It has been converted into the form melting at 68°, but the reverse change has not been effected. E. G.

Chromoisomerism and Homochromoisomerism of Azophenols. ARTHUR HANTZSCH (*Ber.*, 1910, **43**, 2512—2516).—Anhydrous α-azophenol is green; β-azophenol is dark red (Willstätter and Benz, Abstr., 1907, i, 566). These chromoisomerides, m. p. 216—218° (decomp., corr.), are very similar in physical and chemical properties, like the chromoisomeric nitroanilines (this vol., i, 475). The chromoisomeric α- and β-azophenols each form chromo-

isomeric (yellow, red, and green) alkali salts, which, however, show the same absorption spectra in solution. Also, α- and β-azophenols themselves in solution exhibit the same molecular extinction and the same absorption spectra (the orange tinge of β-azophenol in ether, described by Willstätter, is due to the presence of a little phenylhydrazine). Consequently, the azophenols, and also their salts, form homochromoisomerides in solution. This behaviour, examples of which have hitherto been furnished only by stereoisomerides, is further evidence of the *syn*- and *anti*-configurations of the α- and β-azophenols suggested by Willstätter. C. S.

The Nitration of Diazonium Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 224387).—The nitration of diazonium salts frequently yields nitrophenolic compounds, but if the diazotisation is effected in somewhat concentrated sulphuric acid and the solution (or suspension) subsequently treated with nitric acid, or a nitrating mixture, the corresponding nitrated diazonium salts are produced. α-Naphthylamine-5-sulphonic acid (23 parts) was dissolved in concentrated sulphuric acid (200 parts) and treated with nitrosylsulphuric acid (13 parts), dissolved in 50 parts of concentrated sulphuric acid, the mixture stirred, and the temperature maintained at 10—20° during several hours; it was then treated with potassium nitrate (11 parts), when the partly separated diazonium compound redissolved, and, on careful dilution, the nitrated product slowly separated in orange-yellow crystals. F. M. G. M.

The Changes Produced by Urea in the Internal Friction and Electrical Conductivity of Protein Solutions. G. MORUZZI (*Biochem. Zeitsch.*, 1910, **28**, 97—105).—The addition of urea to a protein solution in small concentration at first produces a decrease of conductivity, for as a non-electrolyte, it lessens the movements of ions. Later, or in the case of greater concentrations within a few minutes, conductivity, rises owing to the formation of ammonia. Ammonia can also be detected by Nessler's reagent. Ammonium cyanate acts in the same way. Protein acts in this way in virtue of its being a pseudo-base. Urea is believed to owe its hæmolytic power, and its capacity to unite with complement, to the liberation of ammonia in fluids which contain protein. W. D. H.

Action of Alkalis on Protein. III. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1910, **68**, 165—169. Compare Abstr., 1909, i, 542).—Gelatin was digested with $0{\cdot}5N$-sodium hydroxide solution for seven to nineteen days, then precipitated with tannic acid containing a little sodium chloride (precipitate 1), and the filtrate saturated with sodium chloride (precipitate 2). To remove the sodium chloride from the filtrate, this was precipitated with phosphotungstic acid, the resulting precipitate decomposed with barium hydroxide, and the peptone derivatives precipitated by Kossel's silver nitrate–barium hydroxide method (precipitate 3), and, after removal of silver nitrate, the filtrate was precipitated with phosphotungstic acid, the latter removed, and the filtrate precipitated

with sodium bismuth iodide solution (precipitate 4). The precipitants were removed from each of the four precipitates by making use of acetone solutions, and then the precipitates were hydrolysed with 33 per cent. sulphuric acid. The precipitates before hydrolysis gave glycine, *dl*-ornithine, and *l*-valine. After acid hydrolysis, *dl*-histidine, *dl*-arginine, *d*-lysine, and proline were isolated. The action of alkalis on gelatin is thus similar to its action on clupein. Certain groups of the protein molecule are sensitive to racemisation so long as they are not united as "intraprotein." When the gelatin which has been partly racemised by alkali is subjected to acid hydrolysis, certain groups are racemised and others remain in the active form. The ornithine group especially appears to be readily racemised. J. J. S.

The Amino-acids Obtainable by the Total Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1910, **68**, 477—486).—A general account of the methods adopted and results obtained by the author and others is given. The paper also contains some new details of analytical results, and replies to criticisms.
W. D. H.

The Behaviour of Commercial Egg-albumin to Hydriodic Acid. THEODOR WEYL (*Zeitsch. physiol. Chem.*, 1910, **68**, 236—242). —The name *iodalbose* is given to the product obtained by the action of hydriodic acid on egg-albumin; the iodine is firmly held, and the passage of ammonia through an alcoholic solution of iodalbose still leaves an iodine containing residue which differs from iodalbose mainly in containing less carbon; it is termed *apoiodalbose*. By treatment with zinc, an iodine-free substance, *redalbose*, is obtained, which resembles the original egg-albumin closely in composition. Elementary analyses are given throughout. W. D. H.

The Union of Iodine in Iodothyreoglobulin. ADOLF OSWALD (*Arch. exp. Path. Pharm.*, 1910, **63**, 263—269. Compare Abstr., 1909, i, 123).—All hydrolytic agencies (boiling with acids or alkalis, action of the enzymes trypsin, erepsin, autolase) split off iodine from iodothyreoglobulin in an ionised condition as soon as the protein molecule is broken up into its final cleavage products. A part of the molecule is easily decomposed in this way, and readily yields up its iodine; another part is more resistant. W. D. H.

Hordein and Bynin. A Contribution to our Knowledge of the Alcoholic Extracts of Barley and Malt Albumin. WILHELM KRAFT (*Zeitsch. ges. Brauwesen*, 1910, **33**, 193—195. Compare Abstr., 1907, i, 666; 1908, i, 69).—An account of experiments on the extraction and reactions of hordein and bynin as obtained from malt and barley meal.

Methods of analysis, by hydrolysis and estimation of the decomposition products, are described, and the results compared with those obtained by Osborne and other workers; the two substances were found to resemble each other very closely, but the great difficulty of obtaining them pure rendered the interpretation of results very difficult. F. M. G. M.

Thrombin, Antithrombin, and Prothrombin. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1910, **26**, 453—473).—Thrombin was prepared by extracting washed fibrin with 8% sodium chloride solution, and then precipitating coagulable protein with chloroform. It is soluble in water, is not coagulated by boiling in neutral solutions, it gives the majority of the protein colour tests, and contains no phosphorus or sulphur. When allowed to remain in solution, especially at a high temperature, it gradually loses its power of coagulating fibrinogen. If putrefaction occurs, its coagulating power is at first increased and then lost. Saline solutions may be boiled without losing completely their coagulating power; dialysed solutions are more rapidly and completely destroyed by high temperatures. It keeps indefinitely when dried. Increasing amounts of thrombin give increasing amounts of fibrin, although in decreasing proportion. The weight of fibrin produced by a given submaximal amount of thrombin is not affected by the time during which the thrombin is allowed to act.

The conclusion drawn is that thrombin is probably not an enzyme. One part of thrombin can convert at least two hundred and fifteen times its weight of fibrinogen into fibrin. In the non-coagulable "peptone plasma" of the dog, it is antithrombin which prevents the action of thrombin. This anti-substance is destroyed at 75—80°, but not at 60°. Dilution with water causes spontaneous coagulation in "peptone plasma"; dilution with normal saline solution has no such effect. Prothrombin can be converted into thrombin in solutions free from calcium salts. One experiment is recorded of intravenous injection of large quantities of thrombin; no result followed. W. D. H.

New Method for the Preparation of Crystals of Blood Colouring Matter. J. OFFRINGA (*Biochem. Zeitsch.*, 1910, **28**, 106—111).—Methods previously employed for the preparation of pure hæmoglobin involve the action of heat, solvents, etc., on the blood. The author believes that these processes are not without influence on the labile hæmoglobin, and in any case crystal formation is very slow. He therefore mixes the corpuscles with kieselguhr, and submits the mass to hydraulic pressure. A fairly concentrated hæmoglobin solution is thus obtained, which, in the case of horse-blood, is frozen solid and centrifugalised until again fluid, when a fair crop of crystals is left. The solution from pig's blood required previous concentration in an air current. The purity of the crystals was established by measurement of the extinction coefficients with the spectrophotometer. In each case the ratio 1·59 was obtained, agreeing closely with the Hüfner figure, 1·578, for oxyhæmoglobin. C. D.

The Refractive Indices of Solutions of Certain Proteins. II. The Paranucleins. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, **8**, 287—296. Compare this vol., i, 526).—The collective term paranuclein is applied to an insoluble substance which results from the incomplete peptic hydrolysis of casein, and also to the substance which is formed by high concentrations of pepsin from the synthetic products of complete casein hydrolysis. Additional confirmation of

the view that the substances are identical is obtained by a study of their refractive indices (this vol., i, 526), the value of *a* being 0·0014.

W. D. H.

Comparative Investigation on the Composition and Cleavage Products of Different Silks. X. Monoamino-acids of the Cocoon of the Italian Silk-worm. GEORG ROOSE. **XI. The Mono-amino-acids of the Cocoon of the Japanese Silk "Haruko."** AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, 68, 273—274, 275—276).—The following table gives the results in percentages with the two kinds of cocoon (freed from "gum") employed, calculated on the ash-free substance.

	Italian.	Japanese.
Glycine	33·5	35·0
Alanine	20·0	22·6
Leucine	0·75	0·7
Serine	1·9	0·7
Aspartic acid	1·0	1·0
Glutamic acid	0·25	0·07
Phenylalanine	1·2	1·3
Tyrosine	9·0	9·7
Proline	0·8	0·7

W. D. H.

Partial Hydrolysis of Proteins. II. Fibrinheteroproteose. PHŒBUS A. LEVENE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1910, 8, 269—284).—Heteroproteose was prepared from fibrin by a combination of Kühne's and Pick's methods; it contained C 49·52%; H 6·64%, and N 16·46%, which figures agree very well with Pick's. The results of hydrolysis in parts % are as follows:

Glutamic acid	9·51	Aspartic acid	4·73
Leucine	3·05	Glycine	0·15
*iso*Leucine	2·96	Tyrosine	3·48
Valine	3·54	Arginine	6·35
Alanine	3·39	Histidine	1·76
Valine-alanine mixture	1·86	Lysine	4·80
Proline	4·27	Cystine	4·10
Phenylalanine	2·45	Ammonia	1·65
		Total	58·05

W. D. H.

The Study of Enzymes by means of the Synthetical Polypeptides. ARTHUR H. KOELKER (*J. Biol. Chem.*, 1910, 8, 145—175).—*r*-Alanylglycine can be used with great accuracy for the study of proteolytic enzymes, using the optical method. Solutions of *d*-alanyl-*d*-alanine and of *r*-alanylglycine remain unchanged in solution at 15—20° for thirteen months if toluene is used as a preservative. Buchner's grinding method yields the most active enzymes; precipitation with alcohol cannot be used with advantage in the purification of the active principle. The active principle of yeast which hydrolyses alanylglycine dialyses through parchment. The

solution of the enzyme, freed from most of the solids by dialysis, can be evaporated to dryness and redissolved without impairing its activity. The enzyme is still present after thirteen days' digestion at 37°; heating to 75° for a few minutes destroys it completely. Sodium chloride has no influence on the rate of hydrolysis; calcium chloride in concentration 0·1% increases, and in concentration 1% inhibits, the hydrolysis. W. D. H.

Isoelectric Constant of Pepsin. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1910, **28**, 1—6).—From electrometric measurements of the changes in the hydrogen-ion concentration which are brought about by the passage of a current through solutions of pepsin containing hydrogen ions in gradually diminishing quantities, the authors have obtained the so-called isoelectric constant of pepsin. This is the hydrogen-ion concentration for which the positive and negative ions of the amphoteric electrolyte are equal, and the sum of the ions has a minimum value. The value found is $5 \cdot 5 \times 10^{-3}$. For hydrogen-ion concentrations greater than this, the pepsin migrates to the cathode, and for smaller concentrations towards the anode. If the acidity is much greater than that corresponding with the isoelectric constant, the same effect is found as in the neighbourhood of the isoelectric point. This is attributed in the case of hydrochloric acid solutions to the formation of undissociated pepsinium chloride in presence of the excess of acid. H. M. D.

Action of Pepsin and Hydrochloric Acid. EMIL ABDERHALDEN and EUGEN STEINBECK (*Zeitsch. physiol. Chem.*, 1910, **68**, 293—311).—Gastric juice and hydrochloric acid of the same strength were allowed to act on peptone from various sources, and the result estimated polarimetrically; no change was produced in times varying from one to 170 hours. In similar experiments on native proteins after treatment with gastric juice or hydrochloric acid alone of the same concentration, no effect was observed in either case by the optical method. When solid, denaturalised protein was employed; hydrochloric acid alone produced little or no effect, but gastric juice caused a rise in rotation. If the solidified protein is placed for a short time in gastric juice, washed, and then placed in distilled water, the water after a time at 37° showed evidence of the presence of peptone by the biuret reaction and the polarimeter. W. D. H.

The Action of Sodium Fluoride on Pepsin and Trypsin. ALBERT J. J. VANDEVELDE and EDM. POPPE (*Biochem. Zeitsch.*, 1910, **28**, 134—137).—Amberg and Loevenhart showed that fluorides retard the action of lipase (Abstr., 1908, i, 235), but in the concentrations used they have no effect on the digestive activity of pepsin and trypsin. W. D. H.

Leucoprotease and Anti-leucoprotease. C. H. BURTON BRADLEY (*J. Hygiene*, 1910, **10**, 209—230).—Lympho-protease is a pepsin-like enzyme associated with mono-nuclear leucocytes. Leucoprotease is a trypsin-like enzyme associated with polynuclear leuco-

cytes, and was in the present experiments obtained from pus cells. Experiments on its rate of action are given. It acts only in neutral or faintly alkaline media. The anti-tryptic action of serum varies in different animals, and in the same animal under different conditions (disease, etc.). In the present experiments, the variation in mammals was slight, and immunisation with leucoprotease caused only a small increase of anti-tryptic activity. Goats were the animals used.

W. D. H.

The Erepsin of the Cabbage (Brassica oleracea). Alice F. Blood (*J. Biol. Chem.*, 1910, **8**, 215—226).—An active solution of a vegetable erepsin can be prepared from the cabbage by the ammonium sulphate method; the solution deteriorates very slowly if kept cool. It splits off tryptophan from Witte's peptone and from casein, and tyrosine from "peptone Roche." It clots milk and liquefies gelatin. It does not digest fibrin, egg-white, or edestin in neutral, acid, or alkaline media, or in the presence of hydrocyanic acid. It is active over a considerable range of acidity and alkalinity, but is inhibited by a concentration of hydrogen ions corresponding with the acidity of methyl-orange. W. D. H.

Some Peculiarities of the Proteolytic Activity of Papain. Lafayette B. Mendel and Alice F. Blood (*J. Biol. Chem.*, 1910, **8**, 177—214).—The digestion of Witte's peptone by papain in the presence of the common antiseptics, judged by the tryptophan test, is very slow. Hydrocyanic acid, however, as Vines pointed out, accelerates proteolysis. The same accelerating effect is noticed when other proteins are digested by papain; it also accelerates the clotting of milk and liquefaction of gelatin. Whether there is more than one enzyme in papain is discussed. Hydrogen sulphide also accelerates the digestion. Hydrocyanic acid is provisionally placed with the co-enzymes. Another peculiarity of papain digestion is that digestion proceeds rapidly even after mixtures of the protein and enzyme have been boiled, and plant proteins are rapidly digested at 80°. Spontaneous deterioration occurs rapidly in solutions of papain; egg-white protects papain in some measure. Extracts of *Ascaris*, which are strongly antipeptic and anti-tryptic, exert no inhibition over papain proteolysis.

W. D. H.

Chemical Composition and Formation of Enzymes. II. Hans Euler and Beth af Ugglas (*Arkiv. Kem. Min. Geol.*, 1910, **3**, No. 34, 1—12. Compare this vol., i, 345).—I. *Variation of Enzyme Content of Brewer's Yeast.*—No difference was found in the amount of invertase extracted from yeast dried (1) by treatment with absolute alcohol, (2) by treatment with 95% alcohol, (3) by drying in a vacuum at 40°, and (4) dried at 40° and subsequently slowly heated up to 80°. Yeast cultivated for several generations on dextrose-peptone contained about half as much invertase as the same yeast cultivated in sucrose-peptone. A yeast kept some days under toluene water and subsequently dried, had a low inverting power; the same yeast kept in yeast water and 0·5% sucrose, and strongly aerated, had a normal inverting power.

The diastatic power of barley corns germinated in the one case on moist sand, and in the other on sand moistened with $N/10$-disodium phosphate solution, was in the ratio 1 : 2·3. The increase is attributed to the formation of a co-enzyme from the absorbed phosphate.

II. *Adsorption of Nitrogenous Substances.*—Iron and aluminium hydroxides adsorb proteins, but are not suited for the separation of protein and peptone. Charcoal entirely adsorbs peptone from solution, whilst from yeast extract it adsorbs both nitrogenous and nitrogen-free compounds. From erythrodextrin solutions about 90% is adsorbed by charcoal. Pectic acid is hardly adsorbed by kaolin, strongly by charcoal. Kaolin adsorbs the carbohydrates from yeast-extract preferentially to the nitrogen compounds. The peptones may be removed by charcoal, but the larger part of the nitrogenous constituents still remains. E. F. A.

Inversion of Sucrose by Invertase. V. Destruction of Invertase by Acids, Alkalis, and Hot Water. C. S. Hudson and H. S. Paine (*J. Amer. Chem. Soc.*, 1910, **32**, 985—989).—It has been shown in an earlier paper (this vol., i, 601) that invertase is destroyed by both acids and alkalis at 30°; in each case, the destruction begins at a concentration of about $0·01N$, and becomes almost instantaneous at about $0·05N$. It is now found that as the temperature is raised, the rate of destruction by acids and alkalis increases, and that at about 60° water itself slowly destroys the enzyme, and at 65° the destruction is quite rapid. The destruction of invertase by hot water is evidently due to the same cause as its destruction by acids and alkalis, namely, the hydrolysis of the complex enzyme molecule. The rates of destruction in the same medium at different temperatures are compared, and the coefficients of the rates of increase for 10° rise of temperature are recorded. The average value of this coefficient is 3·1, which agrees with the general observation that this factor for most chemical reactions is between 2 and 4. The hydrolytic destruction of invertase by acids, alkalis, and hot water thus accords with the common types of chemical reactions.

It is shown that lævulose has a remarkable power of protecting invertase from destruction. The rate of destruction by $0·04N$-hydrochloric acid, $0·03N$-sodium hydroxide, 50% alcohol, and hot water was first determined in the absence of the sugar and then with it present in concentrations of 2·7, 5·4, and 10·9%. The results are tabulated and plotted as a curve. This protective action of lævulose can be best explained by assuming that the enzyme forms a compound with the sugar which is more resistant to the action of acids, alkalis, hot water, and alcohol than is invertase itself. E. G.

Inversion of Sucrose by Invertase. VI. Theory of the Influence of Acids and Alkalis on the Activity of Invertase. C. S. Hudson (*J. Amer. Chem. Soc.*, 1910, **32**, 1220—1222).—It has been shown in earlier papers (this vol., i, 601; preceding abstract) that invertase is inactive in alkaline solutions, whilst in presence of dilute acids the activity rises to a maximum and afterwards decreases

with increasing acidity. These phenomena are most readily explained on the assumption that acids and alkalis combine with invertase in accordance with the law of mass-action, and thus prevent it from effecting the inversion of sucrose. On this hypothesis, a formula has been deduced by means of which the activity of invertase has been calculated over a considerable range of acidity and alkalinity. The results thus obtained agree closely with the observed activities.

E. G.

Inversion of Sucrose by Invertase. VII. Effect of Alcohol on Invertase. C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1910, **32**, 1350—1357).—The work described in this paper was carried out with the object of ascertaining the influence of alcohol of various concentrations on invertase at 30°. The observation of O'Sullivan and Tompson (Trans., 1890, **77**, 927), that the activity of invertase is reduced by alcohol, is confirmed, and it is found that the relation between the strength of the alcohol and the activity of the enzyme may be represented as a logarithmic or hyperbolic function.

Invertase is destroyed by alcohol of certain strengths. The destruction follows the course of unimolecular reactions; it is not appreciable if the alcohol is under 20%, is almost instantaneous at 50%, and then decreases to nearly zero at 80%. The rate of destruction is greatly retarded by the presence of sucrose, 6% of the sugar reducing the rate in 50% alcohol to about 1% of its original value. An equation is given expressing the rate of inversion of sucrose by invertase in presence of sufficient alcohol to effect the slow destruction of the enzyme, and is found to yield results agreeing closely with those obtained by experiment. In this way the activity of invertase has been determined in 50% and 60% alcohol.

Invertase can be precipitated by alcohol of about 90% strength without much being destroyed, and a preparation has been thus obtained with 78% of the activity of the original solution. In presence of sucrose very little invertase is destroyed, even when precipitated with 70% alcohol; by this method the enzyme has been recovered with 94—96% of the original activity.

E. G.

The Invertase of Malt Extracts. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1910, **28**, 131—133).—The extract of green malt inverts sucrose. Illustrative experiments are given.

W. D. H.

Existence of a Specific Methylglucase in Beer Yeast. BRESSON (*Compt. rend.*, 1910, **151**, 485—487. Compare Bierry, Abstr., 1909, ii, 747).—Top-fermentation yeast hydrolyses α-methylglucose, whilst bottom-fermentation yeast does not. The author considers that an extract of the former contains a specific diastase not identical with invertin or maltase.

W. O. W.

Preparation of the Polypeptolytic Ferment of Yeast. A. H. KOELKER (*Zeitsch. physiol. Chem.*, 1910, **67**, 297—303).—Whilst the filtered liquid obtained from yeast after treatment with chloro-

form very rapidly causes the hydrolysis of sucrose, it was found that alanylglycine is very slowly hydrolysed by the liquid, which is distinctly acid. When, however, calcium carbonate is added, much carbon dioxide is given off, and the liquid becomes very active, far more so than freshly-prepared expressed yeast.

The liquid is prepared by intimately mixing yeast (500 grams) and precipitated calcium carbonate (30 grams) and adding chloroform (30 c.c.). The yeast liquefies in one to three hours, and is then left for three to four days at the ordinary temperature and filtered. After treating with toluene, it is kept at 38° for auto-digestion until the rotatory power becomes constant (ten to forty hours). When filterod it is ready for use.

Calcium chloride does not increase the hydrolytic activity.

N. H. J. M.

Amylase (Diastase). ALFRED WOHL and E. GLIMM (*Biochem. Zeitsch.*, 1910, **27**, 349—375).—The results of experiments on the effect of maltose and other sugars in checking the production of sugar from starch by amylase showed that the union of sugar with the enzyme increases with the concentration of the solution, and is sufficiently complete in 15% maltose solutions to render the production of sugar inappreciable. Similar results were obtained with 10% dextrose solutions, whilst 15% dextrin solution only reduced the activity of amylase to 25%. Galactose (20%) reduced the action by only one-third, and mannose (10%) by only 15%, whilst sucrose and lævulose had no effect.

Addition of 10% of maltose to solutions of amylase enables the latter to retain its enzymatic power when heated at 60° for ten minutes. The same effect is obtained by addition of 20% of dextrose, invert-sugar, and dextrin, whilst sucrose and starch have less effect. In each case the protective action depends on the concentration, and not on the absolute amount of the substance added.

N. H. J. M.

Amylases. II. Action of Pancreatic Amylase. E. C. KENDALL and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1910, **32**, 1087—1105. Compare this vol., ii, 1011).—A study of the effect of electrolytes and of the concentration of starch on the amylolytic activity of pancreatin. The best commercial preparations are without action on pure starch, but are activated by the addition of neutral electrolytes, or, better, by the action of both a salt and alkali. Below the concentration for maximum activation, the optimum concentrations of salt and alkali depend on each other; above this concentration the optimum for the alkali depends chiefly on the concentration of the starch. Under these conditions, the initial rate of hydrolysis is independent of the amount of starch, but the rate diminishes as the reaction proceeds, the less rapidly the greater the amount of starch present. Equilibrium is attained in 1% starch solutions when the weight of maltose is about 85% of the initial weight of starch. Between 20° and 40°, the temperature-coefficient for amylase conforms to van't Hoff's rule for normal chemical reactions.

Apart from its action as an alkali, asparagine has little effect as an activating agent. W. O. W.

Individuality of Cellase and Emulsin. GABRIEL BERTRAND and A. COMPTON (*Compt. rend*, 1910, **151**, 402—404. Compare this vol., i, 212, 290).—Previous experiments not having definitely established the non-identity of cellase and emulsin, a number of comparative observations have been made on the diastases extracted from almonds, maize, and bran. In each case the material was allowed to act on cellose and on amygdalin, when it was found that the ratio between the rates at which these substances underwent hydrolysis varied very considerably according to the source of the enzymes. It would appear, therefore, that cellase and emulsin are two specific enzymes occurring together in plants in variable proportions. W. O. W.

δ-Emulsin. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, **28**, 408—412. Compare this vol., i, 403).—The action of emulsin on amygdalin occurs in three stages: in the first, mandelonitrile-glucoside and *α*-dextrose are formed; in the second, the first-named substance yields mandelonitrile (*d*-benzaldehyde cyanohydrin) and *β*-dextrose; in the third stage, the first-named substance splits up into benzaldehyde and hydrogen cyanide. The first two stages are hydrolytic, the third is not, and the enzyme responsible for the splitting of the nitrile (oxynitrilase) is distinct from that concerned in hydrolysis (glucosidase). Complete saturation with magnesium sulphate and filtration leads to the appearance in the filtrate of the hydrolytic enzyme only. In precipitation with copper sulphate and half saturation with ammonium sulphate, the filtrate contains both enzymes. The action of oxynitrilase is reversible. W. D. H.

Lipase Reactions. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1910, **8**, 251—264).—When water is present in excess, the hydrolysis of triolein is regularly increased by an increase of lipase; this suggests a mass effect of lipase on the equilibrium of the reaction. A given amount of lipase can under optimum conditions liberate a definite amount of fatty acid from triolein irrespective of the mass of the latter. If more than 50% of water is present, reversion is negligible. Reversion is only appreciable in conditions approaching desiccation. It is possible that lipase, while important in the hydrolysis and absorption of fats, is not important as a factor in their synthesis and storage in the cell. W. D. H.

Action of Acids in the Enzymic Decomposition of Oil by Castor Oil Seeds. YOSHIO TANAKA (*J. Coll. Eng. Tōkyō*, 1910, **5**, 25—42. Compare Armstrong, Abstr., 1906, i, 126).—Castor oil seeds only hydrolyse fats after acid is added. The absolute quantity of the added acid is the important factor, its concentration having no marked influence. The optimum amount of acid required is related to the amount of castor oil seeds alone, and not to the quantity of oil. In the case of mineral and strong organic acids, the optimum quantities

are proportional to their equivalent weights, with weaker organic acids they are larger. The optimum quantity of an acid of the acetic series increases the higher the homologue is; the inhibitory action of an acid when present in excess is greater the lower the homologue.

Lipase is present in castor oil seeds in the form of an insoluble zymogen, which is readily converted by dilute acid into the insoluble enzyme. The added acid does not act by acidifying the medium, but by liberating enzyme from its zymogen. After treating castor oil seeds with acid and completely washing out all the acid and soluble matter with water, a residue was obtained which hydrolysed fatty oils in neutral solution. This proves lipase to be insoluble and active in a neutral medium. It is less active in the presence of free acid, and inactive in an alkaline medium. E. F. A.

Filtration of Rennet and Pepsin. CASIMIR FUNK and ALBERT NIEMANN (*Zeitsch. physiol. Chem.*, 1910, 68, 263—272).—A complete parallelism between the actions of the two enzymes rennet and pepsin was found; they behaved exactly in the same way in attempts to separate them by Holder's filtration method. W. D. H.

Inactivation of Rennet by Shaking. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physiol. Chem.*, 1910, 68, 317—343. Compare this vol., i, 83).—A solution of rennet inactivated by shaking recovers its activity after about an hour. The cause of the inactivation is the concentration of the enzyme on the surface of the froth; on remaining quiet, the former condition of things once more obtains. If the froth is removed after shaking, reactivation does not occur in the residual fluid. There is never a complete return of activity, part of the enzyme disappearing; the non-reversible part of the inactivated rennet increases the longer the shaking is continued; this is regarded as an adsorption phenomenon. W. D. H.

The Milk-curdling and Proteolytic Action of the Gastric Infusion of Ox and Calf and of Natural Gastric Juice. A RAKOCZY (*Zeitsch. physiol. Chem.*, 1910, 68, 421—463).—The milk-curdling enzyme spoken of as chymosin is not identical with pepsin; the former is easily destroyed by incubating at 40° with dilute hydrochloric acid. The two enzymes can also be separated by dialysis, pepsin being almost completely precipitated, whilst the chymosin remains mainly in solution. Chymosin can be extracted from the stomach with water or very dilute hydrochloric acid; a stronger acid then dissolves out the pepsin. The milk-curdling power of gastric juice is due partly to chymosin, partly to pepsin. The amount of the former enzyme lessens with age, so that in the ox the milk-curdling power is due to pepsin alone. Bang's parachymosin is possibly identical with pepsin. W. D. H.

Theory of the Action of Oxydases. ALEXIS BACH (*Arch. Sci. phys. nat.*, 1910, [iv], 30, 152—164).—A polemical summary of

the rival theories of the action of oxydases of Bertrand and of Bach. Colloidal aluminium hydroxide and, to a less extent, other aluminium salts accelerate the transformation of the red oxidation product, produced by the action of tyrosinase on tyrosine, into black melanin. Laccase acting on pyrogallol produces a yellow coloration; the solution in time becomes reddish-brown, and deposits crystals of purpurogallin The addition of a few drops of a solution of an aluminium salt at the yellow stage greatly facilitates the formation of purpurogallin, and the rate of oxidation is the same in a portion of the solution which was boiled to destroy the oxydase. The influence of metallic salts on oxydases is analogous to that of ferrous sulphate on peroxides; the salts are only enabled to act because the oxydase has formed a peroxide. Inorganic salts are not an integral part of oxydases, and do not constitute their active principle; their function is solely to accelerate the oxidising action of the peroxides formed by the true oxydases. E. F. A.

Peroxydase Character of Oxyhæmoglobin. JULES WOLFF and E. DE STOEKLIN (*Compt. rend.*, 1910, **151**, 483—485. Compare Abstr., 1908, i, 490, 573, ii, 1022; 1909, i, 347).—The authors have indicated previously the resemblance between certain colloidal compounds of iron and the peroxydiastases of vegetable origin. Oxyhæmoglobin is now shown to share this similarity, and it has been found by quantitative experiments on the oxidation of potassium iodide, in the presence of hydrogen peroxide, that its catalytic activity surpasses that of the plant peroxydases. It is extremely sensitive to the influence of other substances in the medium, and loses its activity when the solution is boiled. The best results were obtained in an $N/20$-solution of sodium citrate; small quantities of organic acids inhibit the action.

Oxyhæmoglobin shows the usual reactions with pyrogallol, guaiacol, and quinol. The substance appears to be more active after a second crystallisation than after the first. W. O. W.

Isomerisation of Some Phosphorus Compounds. I. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395—420).—The esters of phosphoric acid of the type $P(OR)_3$ under the catalytic influence of alkyl halides are capable of being isomerised into the ethers of the type $PRO(OR)_2$. A rise in temperature of 10° doubles the velocity of reaction, which is also greatest with alkyl iodides and least with the chlorides.

Ethers of the general formulæ $PR'(OR)_2$ and $PR_2'\cdot OR$ (where R is an aliphatic radicle, and R' any other aliphatic or aromatic radicle) also undergo isomerisation when treated with alkyl halides, being converted into derivatives of quinquevalent phosphorus, $PRR'O\cdot OR$ and $O:PRR_2'$ respectively. The velocity of isomerisation is proportional to the mass or concentration of the catalyst, and to the readiness with which the reacting substance forms intermediate additive products; thus the following is the order of the velocity of isomerisation of some of the substances employed: $PR_2'\cdot OEt$, $PR'(OEt)_2$, $P(OEt)_3$.

Phosphenyl chloride, $PPhCl_2$, was prepared by a modification of Michaelis' method (this Journ., 1873, 1148; 1874, 168), a detailed description and figure of the modified apparatus being given; when this substance is heated in a sealed tube at 300°, diphenylphosphoryl chloride, Ph_2PCl, is obtained, which, on treatment in ethereal solution with sodium ethoxide, furnishes *ethyl diphenylphosphinite*, $PPh_2{\cdot}OEt$, b. p. 179°/14 mm., D_0^0 1·0896; the *additive product* with copper iodide has m. p. 190—191°. As a by-product in the formation of the ester, diphenylphosphinic acid, $PPh_2O{\cdot}OH$, is obtained. Under the catalytic influence of ethyl iodide at the ordinary temperature, the ester is converted quantitatively into diphenylethylphosphine oxide, $O{:}PEtPh_2$.

iso*Propyl diphenylphosphinite*, $PPh_2{\cdot}OPr^\beta$, has b. p. 160°/8 mm., D_0^0 1·0925, and forms a crystalline *additive* compound with copper iodide, m. p. 114—115°. iso*Propyl diphenylphosphinate*, $PPh_2O{\cdot}OPr^\beta$, m. p. 95—96°, is formed as by-product in the preparation of the ester On heating at 115° with *iso*propyl iodide, *iso*propyl diphenylphosphinite is quantitatively isomerised into *diphenyl* iso*propylphosphine oxide*, $O{:}PPr^\beta Ph_2$, which crystallises in prisms, m. p. 145—146°.

iso*Butyl diphenylphosphinite*, $PPh_2{\cdot}OC_4H_9$, has b. p. 202—203°/11 mm., D_0^{17} 1·0311, and forms a crystalline *additive* compound with copper iodide. In the preparation of the ester, iso*butyl diphenylphosphinate*, $PPh_2O{\cdot}OC_4H_9$, m. p. 77°, and diphenylphosphinic acid are also obtained. *iso*Butyl diphenylphosphinite, when heated at 120° with *iso*butyl iodide, is isomerised to *diphenyl*iso*butylphosphine oxide*, $O{:}PPh_2{\cdot}C_4H_9$, which forms needles, m. p. 137·5—138°.

Diphenylmethylphosphine oxide, $O{:}PMePh_2$, prepared from diphenylphosphoryl chloride and sodium methoxide, crystallises in needles, m. p. 109—110°, and diphenylmethylphosphine is formed as a by-product. The intermediate ester was not obtained, as it isomerises so rapidly. Similarly, *diphenylbenzylphosphine oxide*, m. p. 192—193°, is obtained from diphenylphosphoryl chloride and sodium benzyloxide. Diethyl phenylphosphinite, $PPh(OEt)_2$, in contact with ethyl iodide is isomerised into *ethyl phenylethylphosphinate*, $PEtPhO{\cdot}OEt$, b. p. 162—164°/16 mm. On hydrolysis, *phenylethylphosphinic acid*,

$$PEtPhO{\cdot}OH,$$

m. p. 79—80°, is formed, of which the barium and silver salts are described. Z. K.

Preparation of Amino-derivatives of Hydroxyarylarsinic Acids and Their Reduction Products. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 224953. Compare Abstr., 1909, i, 347).—It is found that the therapeutically active hydroxyarylarsinic acids can be nitrated, and subsequently reduced to the corresponding amino-compounds having enhanced medicinal value.

Nitrophenolarsinic acid is prepared by dissolving sodium *p*-hydroxyphenylarsinite (144 parts) in 450 c.c. of concentrated sulphuric acid, and slowly dropping in a mixture of 39 c.c. of nitric acid (D 1·4) with an equal volume of concentrated sulphuric acid, with continual stirring and at a temperature of 0°; the mixture is diluted with 1250 c.c. of

water, from which the product separates as a yellow powder. The *alkali* salts are readily soluble in water, yielding deep yellow solutions.

Aminophenolarsinic acid is prepared by the reduction of the foregoing nitro-compound with either sodium amalgam or sodium hyposulphite; it forms minute prisms or leaflets, which blacken and decompose at about 170°.

Diaminoarsenophenol, a yellow powder, is formed by the energetic reduction of nitrophenolarsinic acid with a large excess of sodium hyposulphite; by oxidation with hydrogen peroxide, it is converted into aminophenolarsinic acid.

Nitro-o-cresolarsinic acid, $OH{\cdot}C_6H_2Me(NO_2){\cdot}AsO_3H_2$, prepared from *o*-cresolarsinic acid, is a yellow, crystalline powder, sparingly soluble in cold, readily in hot, water.

Amino-o-cresolarsinic acid is exceedingly soluble in water.

Diaminoarsenocresol, m. p. 165—167° (decomp.), is sparingly soluble in water and in organic solvents.

Dinitrophenolarsinic acid is prepared by the action of excess of nitric acid (D 1·5) with concentrated sulphuric acid on *p*-hydroxyphenylarsinic acid at a temperature of 15—20°; it forms dark yellow leaflets, sparingly soluble in cold, readily in hot, water.

Diaminophenolarsinic acid, silver grey needles, decomposes at about 170° without fusion.

Tetraminoarsenophenol, a bright yellow powder which blackens and decomposes at about 155—157°, is obtained by the reduction of dinitrophenolarsinic acid with a large excess of sodium hyposulphite.

F. M. G. M.

Preparation of Pyrimidine Derivatives containing Mercury. FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 224491).—When the alkali salt of 4-imino-2 : 6-diketodihydropyrimidine-3-acetic acid, $CO{<}{\begin{matrix}NH\text{——}CO\\CH_2{\cdot}C(:NH)\end{matrix}}{>}N{\cdot}CH_2{\cdot}CO_2Na$, is shaken in aqueous suspension with freshly precipitated mercuric oxide or mercury acetamide during several hours, the solution filtered, concentrated in a vacuum, and treated with alcohol, a *compound*,

$$CO{<}{\begin{matrix}NH\text{——}CO\\CHg{\cdot}C(:NH)\end{matrix}}{>}N{\cdot}CH_2{\cdot}CO_2Na,$$

is obtained. It is insoluble in organic solvents, but readily soluble in water, and from which mercury is not precipitated on the addition of sodium carbonate. F. M. G. M.

Organic Chemistry.

Molecular Rearrangements of Carbon Compounds. C. G. Derick (*J. Amer. Chem. Soc.*, 1910, **32**, 1333—1350).—A general paper of a theoretical character, dealing especially with rearrangements of the non-reversible type, such as the transformation of Δ^{β}-unsaturated acids into their Δ^{α}-isomerides. A discussion is given of the formation, stability, and velocity of rearrangement of compounds of this class, and a system of classification of molecular rearrangements of organic compounds is presented. E. G.

Wax Oil. Thor Ekecrantz and E. Lundstrom (*Arch. Pharm.*, 1910, **248**, 500—513).—At the present time wax oil (*oleum cerae*) is always prepared by the dry distillation of wax and calcium oxide. The authors have examined wax oil obtained by three different methods: (*A*) pure beeswax and twice its weight of calcium oxide are distilled in an iron retort, the distillate being rectified by two distillations with twice the quantity of calcium oxide; (*B*) equal weights of beeswax and calcium oxide are distilled in a glass retort on a sand-bath, the distillate being rectified by a second distillation with an equal weight of calcium oxide; (*C*) wax oil prepared in an apothecary's laboratory, and guaranteed unadulterated. *A* is a greyish-yellow mass of crystalline leaflets, and has m. p. 34·5°, $D^{34·5}$ 0·792, acid number 15·4, and iodine number 68·3. *B* is a brownish-yellow oil, having D^{20} 0·792, acid number 8·7, and iodine number 84·3. *C* is also a brownish-yellow oil, having D^{20} 0·790, acid number 9·7, and iodine number 86·6. The oils are distilled with steam, and the residues are separated by acetone into a liquid and a solid portion; from the proportions of the liquid volatile with steam, the liquid non-volatile with steam, and the solid, it is evident that in the distillation of wax and calcium oxide the decomposition of the initially-formed products is least in the oil prepared by method *A* and greatest in that prepared by method *B*. The liquid volatile with steam consists chiefly of a mixture of saturated and unsaturated hydrocarbons, containing 10—16 atoms of carbon; the non-volatile liquid, of a similar mixture containing 16—27 atoms of carbon. The solid portion, m. p. 58—59°, iodine number 13·1, is separated by ether into two parts; one, sparingly soluble in ether, consists chiefly of nonocosane and a little myricyl alcohol; the other, easily soluble in the solvent, is probably a mixture of nonacosane, pentacosane, and a small quantity of unsaturated hydrocarbons. Several commercial wax oils have also been examined. The authors state that the sp. gr. of a wax oil should lie between 0·790 and 0·792, the acid number between 8 and 12, and the iodine number between 80 and 90. They recommend that the iodine number should be determined in the liquid constituents which are volatile with steam. C. S.

Additive Power of 2-Pentene [Δ^{β}-Amylene]. Roger F. Brunel and Eugene G. Probeck (*Amer. Chem. J.*, 1910, **44**, 431—438. Compare Michael, Abstr., 1909, i, 197).—A comparison

is given of the additive power of Δ^{β}-amylene towards acid with that of β-methyl-Δ^{β}-butylene and of α-butylene. Michael's hypothesis regarding the relation between the position of atoms in a molecule and their influence on each other is adopted (Abstr., 1900, i, 321; 1906, i, 550). According to this hypothesis, if one of the unsaturated carbon atoms in the molecule be numbered 1, the mutual influence between this atom and the other atoms of the molecule will decrease according to the scale: 2—3—5—6—4—7—(9—10—11)—8.

In the case of Δ^{α}-butylene and Δ^{β}-amylene this gives:

$$\overset{4\ 3}{\underset{5\ 4}{H_3C}}\cdot\overset{2\ 3}{\underset{3\ 4}{CH_2}}\cdot\overset{1\ 2}{\underset{2\ 3}{CH}}\colon\overset{2\ 3}{\underset{1\ 2}{CH_2}} \qquad \overset{3\ 2}{\underset{4\ 3}{H_3C}}\cdot\overset{1\ 2}{\underset{2\ 3}{CH}}\colon\overset{2\ 3}{\underset{1\ 2}{CH}}\cdot\overset{3\ 4}{\underset{2\ 3}{CH_2}}\cdot\overset{4\ 5}{\underset{3\ 4}{CH_3}}.$$

By an additive process the unsaturated atoms in each molecule are compared, and it is shown that from this consideration alone, the greater additive power should be found in the case of Δ^{β}-amylene, although the difference should not be great. As, however, with the transition from the C_4 to the C_5 series the reduction in the affinity for hydrogen increases, there is a possibility that Δ^{β}-amylene may show the weaker additive power. This is found experimentally to be the case, the ratio being about 7 : 5. A similar comparison with β-methyl-Δ^{β}-butylene shows that the difference in additive power in this case must only depend on the degree of attraction of the negative radicles. Experimentally the velocity with which β-methyl-Δ^{β}-butylene dissolves in dilute sulphuric acid is over one hundred times as great as for Δ^{β}-amylene. N. C.

The Adsorption of Acetylene by Colloidal Palladium. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1910, **43**, 2684—2692).—The liquid hydrosol of palladium, prepared according to the method of Paal and Amberger, dissolves considerable quantities of acetylene. The determination of the amount adsorbed was made in a way similar to that used by Paal and Gerum (Abstr., 1908, ii, 392) to measure the adsorption of hydrogen.

Several days are necessary before the adsorption is complete. After adsorption is complete at room temperature, warming at 40—70°, accompanied by the exercise of a slight pressure, increases the amount of acetylene adsorbed. This extra acetylene is not liberated when the original temperature and pressure are restored, since it is converted partially into volatile and non-volatile condensation and polymerisation products, which, however, could not be isolated in sufficient quantity for identification.

On exposing a palladium hydrosol which has been saturated with acetylene to the air, the chemically unchanged acetylene is set free, especially on warming. On bringing the palladium sol again into contact with acetylene, very little gas is adsorbed, probably because the palladium particles are coated with the acetylene condensation products. This is also the case when the palladium sol is extracted with ether, acidified in order to precipitate the adsorption compound of the solid palladium sol with free protalbic acid, and the precipitate again converted into a liquid sol by the addition of water containing a little sodium hydroxide.

The number of molecules of acetylene adsorbed per gram-atom of

palladium varied from 0·44 to 1·90 molecules, namely, from 1075 to 4690 volumes of acetylene per one volume of palladium, depending on the duration of the experiment and the concentration of the palladium.

T. S. P.

The Adsorption of Acetylene by Palladium Black. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1910, **43**, 2692—2694).—The adsorption of acetylene by palladium black was measured in an apparatus similar to that used by Paal and Gerum (Abstr., 1908, ii, 392) to determine the adsorption of hydrogen. The palladium was suspended either in an aqueous solution of sodium protalbate or in an aqueous solution of ammonia, or in aqueous alcohol, in order to determine whether the acetylene adsorbed by the palladium reacted with the dissolved substances. In all three cases, approximately equal quantities of acetylene were adsorbed (1·36—1·53 molecules per gram-atom of palladium); in no case did the adsorption exceed that obtained with colloidal palladium under similar conditions.

Some of the adsorbed acetylene was changed into condensation products, but not to the same extent as with colloidal palladium.

T. S. P.

Tetranitromethane. ERNEST BERGER (*Compt. rend.*, 1910, **151**, 813—815. Compare Pictet and Généquand, Abstr., 1903, i, 305, 596; Chattaway, Trans., 1910, **97**, 2099).—The following method is recommended for the preparation of tetranitromethane. A mixture of 160 grams of absolute nitric acid (or 180 grams of fuming nitric acid) with glacial acetic acid (100 grams) is treated, in a flask kept cool under the tap, with acetic anhydride (290 grams). The flask is allowed to remain in cold water for some hours, and then for a night at the ordinary temperature. After heating for three to four hours at 25—30°, the temperature is raised by 5° every three to four hours until it reaches 65—70°, when the liquid is poured into four times its volume of water. The tetranitromethane is washed and dried over anhydrous sodium sulphate; the acid liquid from which it separates contains trinitromethane and trinitroacetic acid. The yield is 28—60 grams, according to the concentration of the nitric acid.

Tetranitromethane has b. p. 21—23°/22 mm., 124—125°/750 mm. with slight decomposition; D^{22} 1·620. The heat of combustion was determined in presence of amyl alcohol, since the compound itself contains too much oxygen. The results are expressed by the equations: $C(NO_2)_4 = CO_2 + 2N_2 + 3O_2 + 89{\cdot}6$ Cal. $C_{\text{diamond}} + 2N_{2(\text{gas})} + 4O_{2(\text{gas})} = C(NO_2)_4 + 4{\cdot}7$ Cal.

W. O. W.

Catalytic Reactions by means of Metallic Oxides. ALPHONSE MAILHE (*Chem. Zeit.*, 1910, **43**, 1173—1174, 1182—1184, 1201—1204).—In these three papers a résumé is given of the results of recent work carried out by the author and others on the catalytic reactions induced by heated metallic oxides. The first paper deals with the decomposition of alcohols, acids, and esters, and records, for the most part, results already published (Senderens, Abstr., 1907, i, 577; 1908, ii, 166; i, 494, 495; 1909, i, 127, 286, 627; and this vol., i, 11, 179, 318, 489; Sabatier and Mailhe, 1908, i, 594, 713; 1909, i, 546, and this vol., i, 294, 606). In the second paper a theory of these catalyses already outlined (*loc. cit.*, but especially 1908, i, 594, and this vol., i,

294) is discussed in detail in its application to various special cases, and the preparation of amines is described (Abstr., 1909, i, 292), with a number of new examples of the application of the process to this class of compounds. The third paper deals with the preparation and decomposition of thiols by this process (this vol., i, 294, 456, 536).

T. A. H.

Two Active Alcohols and a Third Ketone Contained in Cocoanut Oil. ALBIN HALLER and A. LASSIEUR (*Compt. rend.*, 1910, **151**, 697—699. Compare this vol., i, 355).—The odoriferous constituents of the "essence" of cocoanut butter have been shown previously to consist of higher fatty acids with neutral substances. The latter have now been separated into alcohols and ketones by means of phthalic anhydride. The alcoholic portion consists chiefly of d-*methylnonylcarbinol*, b. p. 228—233°, D_4^{23} 0·827, n_{23} 1·4336, $[\alpha]_D + 1°24'$, with a small quantity of d-*methylheptylcarbinol*, b. p. 195—196°, D_4^{25} 0·823, n_{21} 1·4249, $[\alpha]_D + 2°25'$. The ketonic portion contains about 75% of methyl nonyl ketone, together with methyl heptyl ketone and methyl undecyl ketone.

W. O. W.

Basic Properties of Oxygen: Compounds with Bromine and Iodine. DOUGLAS McINTOSH (*J. Amer. Chem. Soc.*, 1910, **32**, 1330—1333).—It has been suggested by Tschelinzeff and Konowaloff (Abstr., 1909, i, 353) that the compound $C_4H_{10}OBr_2$, obtained by the action of bromine on ethyl ether, has the constitution $C_4H_{10}O{<}^{Br}_{Br}$.

It is now stated that the compound obtained by these authors was not pure, and that the value of the molecular weight in acetic acid which they obtained is not trustworthy, since the dibromide is decomposed by this solvent. Attempts have been made to determine the molecular weight of the di- and tri-bromides of ethyl ether by f.-p. measurements in chloroform solution, but without success, since the substance undergoes partial decomposition under these conditions. It has also been found that this constant cannot be determined by Ramsay and Shields' method.

Waentig (this vol., ii, 117) has stated that iodine combines with certain organic solvents at low temperatures. It is now found that when a solution of iodine in alcohol or acetone is cooled to $-80°$ or $-90°$, a substance separates which may be mistaken for a compound. When completely dried at a low temperature, however, the product is shown by analysis to be iodine, contaminated with a little of the solvent. When ethyl acetate is used, mixed crystals of the solvent and iodine may be obtained.

When bromine and chlorine are dissolved in organic solvents containing oxygen, an appreciable amount of heat is developed, whilst, in the case of iodine, a slight absorption of heat occurs. On the basis of these facts, it is shown that it is improbable that iodine compounds could be produced in a reasonably pure state by cooling the solutions to a low temperature.

E. G.

The Solubilities of the Pharmacopœial Organic Acids and Their Salts. ATHERTON SEIDELL (*Bull.* No. **67**, *Hyg. Lab.*, *U.S. Pub. Health and Mar. Hosp. Serv.*, 1910, 7—98).—The importance attached

to the quotation of solubility determinations in pharmacopœial descriptions of chemicals has led the author to re-determine the solubilities of the organic acids of the United States Pharmacopeia in water, aqueous alcohol, and a number of common organic solvents, and to obtain like data for the official salts of these acids as regards water and aqueous alcohol. The results obtained, together with obviously trustworthy results recorded by previous investigators, are tabulated, and also represented graphically in the original.

The method used consisted in agitating the solvent with excess of the acid or salt at the selected temperature, due precautions being taken to secure saturation in each case and to ensure uniform experimental conditions. The specific gravity of the saturated solution was determined, and then the quantity of substance in solution ascertained by evaporation to dryness, or if this was impossible, by chemical analysis. The results are expressed as the number of grams of substance in 100 grams of the saturated solution.

The following deductions are drawn from a consideration of all the results obtained. Of the thirty-five substances examined, only nine gave results showing satisfactory agreement with the figures quoted in the U. S. P., the remainder showing differences ranging from 5 to 100%. A solubility determination is of little value as a criterion of the purity of a substance. It is impossible to predict the solubility of a substance in a mixture of alcohol and water from a knowledge of its solubility in each of these solvents alone. Citric acid shows nearly parallel solubility curves for the anhydrous and hydrated forms in aqueous alcohol, the second being the more soluble substance. Potassium citrate mixed with aqueous alcohol causes the separation of an upper layer of nearly pure alcohol, and a lower layer of aqueous salt solution (compare Linebarger, Abstr., 1892, 1146). Oleic acid shows apparently unstable solubility equilibrium in aqueous alcohol at certain concentrations. Trichloroacetic acid undergoes partial esterification in aqueous-alcoholic solutions. T. A. H.

Organic Salts of Yttrium. SEBASTIAN TANATAR and I. VOLJANSKI (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 586—590).—Yttrium *propionate*, $(EtCO_2)_3Y$, formed by the prolonged heating on a water-bath of yttrium oxide with dilute propionic acid, can be readily obtained pure by recrystallisation. It forms white, monoclinic needles, and is insoluble in all organic solvents except warm alcohol, by which, however, it is converted into the *basic* salt. The following salts were also obtained: the iso*butyrate*, $(C_3H_7{\cdot}CO_2)_3Y$; *lactate*,

$$(OH{\cdot}CHMe{\cdot}CO_2)_3Y,4H_2O;$$

benzoate, $Y(OBz)_3$; *fumarate*, $(C_4H_2O_3)_3Y_2,2H_2O$; *phthalate*,

$$(C_{10}H_4O_4)_3Y_2,C_{10}H_6O_4;$$

crotonate, $(CHMe{:}CH{\cdot}CO_2)_3Y,5H_2O$; *malate*, $(C_4H_4O_5)_3Y_2$; and *citroconate*, $(C_5H_4O_4)_3Y_2,9H_2O$.

Yttrium nitrate, $Y(NO_3)_3,2H_2O$, is formed by dissolving yttrium oxide in excess of dilute nitric acid and evaporating to a syrup, which is dried at 100°. After cooling and stirring, the syrup suddenly forms tiny crystals with development of heat. Z. K.

Transformation of Stereoisomeric Ethylenic Compounds. I. PAUL PFEIFFER (*Ber.*, 1910, **43**, 3039—3048).—When an $\alpha\beta$-dihaloid derivative of butyric or β-phenylpropionic acid is treated with potassium hydroxide, it furnishes the unstable corresponding α-halogenated *iso*crotonic or *allo*cinnamic acid, whereas with pyridine, it yields the stable α-halogenated isomeride. In both cases the unstable form is first produced, but in the presence of pyridine this is transformed into its isomeride.

[With A. LANGENBERG.]—$\alpha\beta$-Dichlorobutyric acid reacts slowly with pyridine at the ordinary temperature, but more rapidly on warming at 100°, to give α-chlorocrotonic acid. Under like conditions, $\alpha\beta$-dibromobutyric acid furnishes α-bromocrotonic acid. $\alpha\beta$-Dichloro-β-phenylpropionic acid is not decomposed by pyridine at atmospheric temperature, but at 100° furnishes α-chlorocinnamic acid, whilst $\alpha\beta$-dibromo-β-phenylpropionic acid gives cinnamic with some α-bromocinnamic acid.

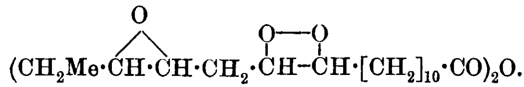
α-Chloro*iso*crotonic acid, when kept in pyridine solution with pyridine hydrochloride at atmospheric temperature, or more rapidly on warming, is converted into α-chlorocrotonic acid, and under like conditions a similar change ensues with α-chloro*allo*cinnamic acid, α-bromo*allo*cinnamic acid, and α-bromo*iso*crotonic acid, the last-mentioned acid being also transformed when kept with pyridine alone. β-Chloro*iso*crotonic acid is not transformed into β-chlorocrotonic acid under these conditions. T. A. H.

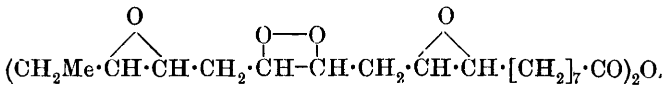
Linolenic Acid and Linseed Oil. ERNST ERDMANN and FRED BEDFORD (*Zeitsch. physiol. Chem.*, 1910, **69**, 76—84. Compare Abstr., 1909, i, 357).—Several miscalculations are pointed out in Rollett's work (Abstr., 1909, i, 760). The general conclusions drawn are: (1) The hydrogen and iodine numbers show that in linseed oil there is not more than 20—25% of acids, $C_{18}H_{30}O_2$, containing three ethylene linkings. This is mainly α-linolenic acid, which yields a hexabromide, m. p. 179°. (2) When the solid hexabromide is treated with zinc, a mixture of two stereoisomeric acids is formed; 75% of this mixture consists of β-linolenic acid and 25% of the α-acid. The β-acid yields an oily tetrabromide, and this with zinc gives the β-acid together with polymerisation and anhydro-products. (3) Rollett's conclusions that only one linolenic acid is present in linseed oil, and that the amount is some 50—60% are incorrect. J. J. S.

The Composition of Boiled Linseed Oil and the Distribution of Oxygen in Dried Layers of Oil. I. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658—676. Compare Erdmann, Abstr., 1909, i, 357).—The solid substances formed when linseed oil is dried on a plate contain unsaturated double linkings, and even when the greatest quantity of oxygen has been absorbed, the dried oil still gives an iodine number not less than 14·15. The amount of oxygen absorbed depends on the thickness of the layer and the surrounding temperature, but in all cases if, after the layer has ceased to increase in weight, the surface of the layer be removed, oxygen commences to be absorbed again and the weight increases.

Although fresh linseed oil has no reducing properties, the oil dried on plates is markedly reducing, owing to the formation of two *linoxins* from the glycerides of linolic and linolenic acid.

The linoxin (I) from linolenic acid is a solid insoluble in alcohol and ether, that (II) from linolic acid is a soluble syrupy liquid. The linoxins are not ozonides, and a detailed study of their properties leads to the conclusion that they have the following constitution :

I. 

II. 

The relative proportions of each formed in various experiments are estimated and found to agree very well with the theoretically calculated numbers. Z. K.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. G. CALCAGNI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 333—337).—By a method analogous to that of Weinland (Abstr., 1909, i, 757), the author has prepared basic salts of hexaglycollato- and hexalactato-trichrome bases. To them is to be assigned a constitution similar to that of the salts obtained by Weinland, so that in this case the alcoholic hydroxyl groups take part in the formation of the salt, whilst other negative radicles (chlorine, bromine) only strengthen the carboxylic hydrogen. The *basic glycollate* of a *hexaglycollatotrichrome base*, $\left[Cr_3\begin{matrix}(CO_2 \cdot CH_2 \cdot OH)_6\\(OH)_2\end{matrix}\right]CO_2 \cdot CH_2 \cdot OH,Cr(OH)_3$, is obtained as a dark green, hygroscopic powder by dissolving chromic hydroxide in glycollic acid and precipitating with alcohol. It is stable towards ammonia and sodium hydroxide; chromic hydroxide is only precipitated after prolonged ebullition with the latter. The *basic lactate* of a *hexalactatotrichrome base*,

$$\left[Cr_3\begin{matrix}(CO_2 \cdot CHMe \cdot OH)_6\\(OH)_2\end{matrix}\right]CO_2 \cdot CMe \cdot OH,Cr(OH)_3,$$

was obtained in the same way, and has similar properties. The analytical results indicate the presence of about $5H_2O$ in the molecule. When it is treated with fuming nitric acid on the water-bath, only one of the lactate groups is replaced, the *nitrate*,

$$\left[Cr_3\begin{matrix}(CO_2 \cdot CHMe \cdot OH)_6\\(OH)_2\end{matrix}\right]NO_3,Cr(OH)_3,$$

being formed. R. V. S.

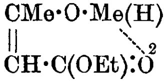
The Equilibrium Isomerism of Acetoacetic Ester and the So-called Isorropesis of its Salts. ARTHUR HANTZSCH (*Ber.*, 1910, **43**, 3049—3076).—A systematic investigation of acetoacetic ester and its homologues has been made both by refractometric (compare Brühl, Abstr., 1905, i, 407) and ultra-violet absorption spectra methods, with a view to determining its constitution. The following are the chief results recorded.

The dialkylacetoacetates, which exist only in the ketonic form, absorb but little ultra-violet light, whilst ethyl ethoxycrotonate shows large absorption, but neither of these exhibits much change in absorption in whatever solvent it is examined. Ethyl acetoacetate, on the contrary, shows great variation in absorption, depending on the solvent used; thus, in water and dilute hydrochloric acid, it is slightly absorbent, whilst in indifferent solvents the absorption increases inversely as the dielectric constant of the solvent, and reaches its maximum in hexane. The absorption also increases with rise of temperature and with increasing dilution, the latter especially in hexane. This rise in absorptive capacity is parallel with Brühl's exaltation of refraction. Methyl- and ethyl-acetoacetic esters show similar behaviour. Homogeneous ethyl acetoacetate shows greater absorption than its solutions.

Tables and graphs illustrating these general results are given in the original.

The following explanation of these results is given. The aceto-acetates and their mono-substitution products, in the homogeneous state and also in solution in indifferent solvents, are equilibrium mixtures of keto-enolic isomerides. The equilibrium point is shifted to the enol side by (1) rise of temperature, (2) dilution in the same solvent, (3) use of solvents of decreasing dielectric constant. Ethyl acetoacetate is strongly enolised and slightly associated. In dilute hydrochloric acid solution, it is practically entirely ketonised, and in dilute hexane solution almost entirely enolised, since then it shows nearly the same absorption spectrum as ethyl ethoxycrotonate. In water, at medium temperatures, it is about one-fifth, and in methyl alcohol about nine-tenths, enolised. These results are confirmed in part by Stobbe's observations on the ferric chloride test (Abstr., 1907, i, 177).

It is pointed out that the phenomenon of isorropesis (Stewart and Baly, Trans., 1906, **89**, 498) is particularly well shown by the addition of alkalis to ethyl acetoacetate (compare Baly and Desch, *ibid.*, 1904, **85**, 1036), and is probably the result of "salt" formation, since maximum absorption is reached more quickly the greater the concentration of ester and the more acidic in nature the latter is. Further, the metallic derivatives of ethyl acetoacetate are optically and chemically different from the enol-form of the ester itself, and in these derivatives the ester must exist in a new form, which may be called the aci-form, since it probably also occurs to a minute extent in solutions of the ester in hexane. The relationship of the aci- and enol forms cannot be that of stereoisomerides, as these would be optically identical (this vol., i, 474), and of the formulæ considered for the aci-form, the most likely is the annexed one, the dotted line indicating a "subsidiary valency." This formula represents a "valency isomeride" of the enol form and permits in a modified way of Baly and Desch's "oscillation" explanation of isorropesis, the oscillation taking place by an interchange of "principal" and "subsidiary" linkings at the points marked 1 and 2, with a suitable change in position of the double linkings. Apart from the equilibrium isomerism



between the keto and enol forms and between the enol and aci-forms, there is a third possible equilibrium between the trans-enol and cis-enol forms, and it seems likely that the cis-enol form only can pass into the aci-form thus :

$$\begin{array}{ccccc} \text{Me·CO} & & \text{Me·C·OH} & & \text{CMe·C·OH(Me)} \\ | & \rightleftarrows & \| & \rightleftarrows & \|\quad\vdots \\ \text{(CO·OEt)CH}_2 & & \text{(CO·OEt)CH} & & \text{H·C·CO·OEt} \\ \text{Keto-form.} & & \text{Trans-enol form.} & & \text{Cis-enol-} = \text{aci-form.} \end{array}$$

T. A. H.

Ethyl *a*-Nitroso*iso*heptoate and the Action of Nitrous Gases on Allyl-, Dimethyl-, and Diethyl-acetoacetic Esters. JULIUS SCHMIDT and AUGUST HAID (*Annalen*, 1910, **377**, 23—30. Compare Schmidt and Widmann, Abstr., 1909, i, 453).—The nitrous gases from a mixture of nitric acid and arsenious anhydride react with ethyl *iso*heptoate, yielding *ethyl a-nitroso*iso*heptoate*,

$$CHMe_2·CH_2·CH_2·CH(NO)·CO_2Et,$$

as a dark blue oil, $D_4^{20·2}$ 1·054, and $n_D^{20·2}$ 1·6251. It has a strong odour, cannot be distilled even under very low pressures, and gives Liebermann's nitroso-reaction. When kept or when treated with water or alkalis, the blue liquid becomes colourless; this is partly due to polymerisation, and partly to conversion into the isomeric oximino-derivative. It has a deeper colour, and is also somewhat more stable than the analogous *iso*hexoate (Schmidt and Widmann). When oxidised with hydrogen peroxide, the nitroso-ester yields *ethyl a-nitro*iso*heptoate*, $CHMe_2·CH_2·CH_2·CH(NO_2)·CO_2Et$, as a yellow oil, D_4^{15} 1·070, n_D^{15} 1·4486.

The nitrous gases react with ethyl allylacetoacetate, but definite products could not be isolated, and when ethyl dimethyl- and diethyl-acetoacetates were used, the unaltered esters were recovered. It would thus appear that substituted acetoacetic esters, in which both the methylene hydrogens are replaced by alkyl groups, cannot yield nitroso-derivatives.

J. J. S.

Esters of Aliphatic Nitroso- and Nitro-carboxylic Acids. JULIUS SCHMIDT and HEDWIG DIETERLE (*Annalen*, 1910, **377**, 30—70. Compare Schmidt and Widmann, Abstr., 1909, i, 453; Schmidt and Haid, preceding abstract).—Nitrous gases from arsenious anhydride and nitric acid are able to replace by nitroso-groups, not merely acetyl, but also formyl and benzoyl groups in esters of *a*-acylated saturated carboxylic acids. The formyl group is replaced most readily, and the benzoyl group least readily. In the last case the reaction requires several days for completion, and the product actually isolated is not a true nitroso-derivative, but the isomeric oximino-compound; at the same time, partial hydrolysis occurs, so that the final product in the case of ethyl benzoylsuccinate is ethyl hydrogen oximinosuccinate, $CO_2H·CH_2·C(:NOH)·CO_2Et$.

The nitro-group in esters of nitro-substituted saturated acids can also be replaced by the nitroso-group by the action of the nitrous gases on the ester in the absence of a solvent, but it has not been found possible, so far, to replace the bromine atom in *a*-brominated

esters by the nitroso-group. When ethyl formylphenylacetate is used, an oximino-group replaces the formyl group, and at the same time the phenyl radicle is nitrated, so that the final product is

$$NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO_2Et.$$

Ethyl diacetylacetate does not react with the nitrous gases; the presence of a CH-group in the acylated ester is thus essential for the reaction (compare preceding abstract), and it is probable that the nitroso-group first replaces the hydrogen atom of this group and that hydrolysis then takes place, resulting in the elimination of a molecule of the organic acid, for example: $CH_3\cdot CO\cdot CHR\cdot CO_2Et \longrightarrow CH_3\cdot CO\cdot C(NO)R\cdot CO_2Et \longrightarrow CH_3\cdot CO_2H + NO\cdot CHR\cdot CO_2Et$.

The changes which the nitroso-derivatives undergo when kept have been examined, mainly by cryoscopic measurements. In the case of ethyl α-nitrososuccinate and ethyl α-nitroso-*n*-butyrate, the blue oils undergo polymerisation, yielding the nearly colourless bimolecular products, which, in their turn, change gradually into the yellow or colourless, unimolecular oximino-derivatives, for example:

$$\underset{\text{Blue.}}{CO_2Et\cdot CH_2\cdot CH(NO)\cdot CO_2Et} \longrightarrow \underset{\text{Nearly colourless.}}{[CO_2Et\cdot CH_2\cdot CH(NO)\cdot CO_2Et]_2} \longrightarrow \underset{\text{Yellow.}}{CO_2Et\cdot CH_2\cdot C(:N\cdot OH)\cdot CO_2Et.}$$

In most other cases the second change begins before the first is complete, so that the molecular weight never reaches the value required for the bimolecular compound. This is extremely well shown in the case of ethyl α-nitrosopropionate, prepared from ethyl α-formylpropionate. The conversion into the oximino-compounds is accelerated to an enormous extent by the presence of minute traces of alkalis, and most solvents, for example, water and benzene, also facilitate the transformation.

Good yields of esters of amino-acids cannot be obtained by reducing either the nitroso- or the more stable nitro-esters, the best results being obtained when stannous chloride and hydrochloric acid are used. Small amounts of the oximino-carboxylic acids can be prepared by hydrolysing the esters of the nitroso-acids with very dilute alkali at low temperatures. Small yields of the potassium salts of the α-nitro-acids are formed when the corresponding esters are treated with concentrated potassium hydroxide solution. They form golden-yellow crystals, and cannot be transformed into the corresponding acids.

Ebert's ethyl α-oximinosuccinate (Abstr., 1885, 1122) is formed readily when ethyl α-nitrososuccinate is shaken with sodium carbonate solution; it has n_D^{18} 1·3765, and when hydrolysed with sodium hydroxide, the oximino-ester yields oximinosuccinic acid, ethyl oximinopropionate, or oxalacetic acid, according to the conditions of the experiment, but in all cases the yields are extremely poor, namely, 1 to 2%.

*Ethyl α-nitroso-*n*-valerate*, $CHEt\cdot CH(NO)\cdot CO_2Et$, prepared from ethyl *n*-propylacetoacetate, forms a dark blue oil, and retains the blue colour for some twelve to twenty-four hours at the ordinary temperature. It has D_4^{20} 1·213 and n_D^{20} 1·4350, and the isomeric α-oximino-ester is a yellow oil, with n_D^{18} 1·3250. When oxidised with hydrogen peroxide, the nitroso-derivative yields *ethyl α-nitro-*n*-valerate*, $CH_2Et\cdot CH(NO_2)\cdot CO_2Et$, as a yellow oil, with D_4^{18} 1·0551, n_D^{18} 1·4595, and has a very strong odour.

Ethyl α-nitrosohexoate (Abstr., 1909, i, 454) has n_D^{20} 1·4515, and when the corresponding nitro-derivative is treated with concentrated potassium hydroxide solution, yellow crystals of *potassium α-nitro-hexoate*, $C_4H_9\cdot CH(NO_2)\cdot CO_2K$, are formed, together with the potassium salt of α-oximinohexoic acid.

α-Oximinohexoic acid, $C_4H_9\cdot C(:N\cdot OH)\cdot CO_2H$, crystallises from water in colourless needles, m. p. 132° (decomp.).

Pure ethyl α-nitrosopropionate, prepared from ethyl α-formyl-propionate, has n_D^{18} 1·4295, and can be kept for two or three days. The best method for transforming it into the isomeric α-oximino-ester is shaking for a few minutes with very dilute sodium hydrogen carbonate solution and keeping for two to three hours.

Ethyl oximinonitrophenylacetate, $NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO_2Et$, crystallises from alcohol in colourless, glistening needles, m. p. 195°. It yields sparingly soluble mercurous and silver derivatives, and gives a dirty reddish-brown colour with ferric chloride. The *benzoyl* derivative, $NO_2\cdot C_6H_4\cdot C(CO_2Et):NO\cdot COPh$, has m. p. 145°, and its *methyl ether* forms colourless needles, m. p. 151°.

It has not been found possible to isolate a nitroso-derivative from ethyl dibenzoylsuccinate by the action of nitrous gases, although benzoic acid is eliminated.

Ethyl α-benzoylpropionate reacts with nitrous gases, yielding ethyl α-oximinopropionate and the corresponding acid (Ebert, *loc. cit.*).

J. J. S.

Synthesis of β-Methyl-αβ-diethylhydracrylic Acid and its Properties. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 891—899. Compare Abstr., 1909, i, 304).—*Ethyl β-methyl-αβ-diethylhydracrylate* [*ethyl β-hydroxy-β-methyl-α-ethylvalerate*],

$$OH\cdot CMeEt\cdot CHEt\cdot CO_2Et,$$

is best prepared by mixing methyl ethyl ketone with ethyl α-bromo-butyrate dissolved in dry benzene, and pouring on to dry zinc previously treated with sulphuric acid. The whole is heated on the water-bath in a reflux apparatus for some hours, after which the product is treated with water, fractionated, and purified. It is a colourless, mobile liquid, b. p. 115·5—116°/25 mm., 214—219°/760 mm. (decomp.), D_4^{23} 0·96230, which with barium hydroxide yields the *acid*, $OH\cdot CMeEt\cdot CHEt\cdot CO_2H$, of which the *potassium*, *sodium*, *barium*, *silver*, and *copper* salts are described.

With sulphuric acid the acid is decomposed, thus:

$$OH\cdot CMeEt\cdot CHEt\cdot CO_2H = H_2O + CMeEt:CEt\cdot CO_2H$$

$$\text{and } OH\cdot CMeEt\cdot CHEt\cdot CO_2H = H_2O + CO_2 + OH\cdot CMeEt\cdot CH_2Et.$$

When the ester is treated with phosphoric oxide, *ethyl β-methyl-α-ethyl-Δ^α-pentenoate*, $CMeEt:CEt\cdot CO_2Et$, b. p. about 188—190°, is formed, which when treated with potassium hydroxide yields β-methyl-α-ethyl-Δ^α-pentenoic acid, $CMeEt:CEt\cdot CO_2H$, of which a *bromide* and the *potassium*, *silver*, *lead*, and *calcium* salts were prepared. Z. K.

The Unary Termolecular Pseudo-ternary System: Acetaldehyde, Paracetaldehyde, and Metacetaldehyde. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 318—329).—Observations relating to the connexion between acet-

aldehyde, paracetaldehyde, and metacetaldehyde are discussed, and it is shown that the apparently contradictory results relating to the conditions under which these substances are formed and transformed into one another can be accounted for on the assumption of a ternary equilibrium represented by :

$$\begin{array}{ccc} \text{Acetaldehyde} & \rightleftarrows & \text{Paracetaldehyde.} \\ & \nwarrow\!\searrow \quad \nearrow\!\swarrow & \\ & \text{Metacetaldehyde.} & \end{array}$$

On account of the conversion of metacetaldehyde into the other two isodynamic forms, previous attempts to determine the triple point of metacetaldehyde have given erroneous results. By a method in which the substance, contained in closed thin-walled capillary tubes, was immersed in baths of different temperatures, the melting point of metacetaldehyde under its own vapour pressure was found to be 246·2°. This is much higher than the temperatures, 184° and 167°, obtained by Roozeboom and Hollman respectively. H. M. D.

The System Acetaldehyde–Alcohol. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 329—339).—Experiments have been made to determine the nature of the additive compounds which are formed in mixtures of acetaldehyde and ethyl alcohol. Mixtures which had been kept at the ordinary temperature for about a year, or heated for several hours at 100°, gave no indication of the presence of water when tested with anhydrous copper sulphate. When acetaldehyde-alcohol mixtures are left in contact with copper sulphate for a long time, a blue colour appears, however, and this is supposed to be due to the catalytic influence of the copper salt on the formation of acetal. This accelerating effect affords a convenient method for the preparation of acetal.

The mixing of acetaldehyde and alcohol is attended by a large diminution in volume, and it is found that the density of an equimolar mixture has a maximum value (D_4^{18} 0·8719) which is very much greater than that of either of the components. The density data indicate therefore the formation of a compound $CH_3\cdot COH,C_2H_5\cdot OH$.

Measurements of the boiling points of various mixtures at different pressures, and of the composition of the vapour emitted by these mixtures, were also made. The curves obtained by plotting boiling points against the composition of the liquid also indicate the formation of the above compound, and a further compound containing a larger proportion of alcohol. Similar conclusions are drawn from the heats of mixing, a maximum heat effect being obtained for an equimolar mixture.

The data obtained in freezing-point measurements confirm these results, and indicate with certainty the formation of compounds, $CH_3\cdot COH,C_2H_5\cdot OH$ and $CH_3\cdot COH,2C_2H_5\cdot OH$, which are considerably dissociated at their respective melting points, $-122°$ and $-123°$.

H. M. D.

Preparation of Keten from Acetone. JULIUS SCHMIDLIN and MAXIMILIAN BERGMANN (*Ber.*, 1910, **43**, 2821—2823. Compare Wilsmore, Trans., 1907, **91**, 1938).—Keten appears to be stable

at fairly high temperatures, and a 14% yield can be obtained by passing the vapour of acetone through a hard glass tube filled with porous earthenware and heated at 500—600°. The decomposition of acetone appears to take place in two stages: (1) at about 500—600°, $2CH_3·CO·CH_3 = 2CH_2:CO + 2CH_4$, and (2) at higher temperatures, $2CH_2:CO = 2CO + C_2H_4$. It is impossible to prevent part of the keten from decomposing even at the lower temperature.

It is highly probable that in the preparation of keten from acetic anhydride, acetone is the first product formed. J. J. S.

A New Sugar, Verbascose, from the Root of Mullein. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1910, **151**, 760—762*).—A description of the detection and isolation of a new polysaccharide occurring in the roots of *Verbascum thapsus*. The sugar, for which the name *verbascose* is suggested, crystallises in minute, spherular aggregates of slender needles, m. p. 219—220°, on the Maquenne block; $[\alpha]_D$ +169·9°. It appears to be analogous to stachyose, since, on hydrolysis, dextrose, lævulose, and galactose are produced. Verbascose does not reduce Fehling's solution; on oxidation with nitric acid, it yields mucic acid.

Verbascum thapsus appears also to contain a glucoside, hydrolysable by emulsin. W. O. W.

Purification of Starch. GIOVANNI MALFITANO and MLLE. A. N. MOSCHKOFF (*Compt. rend.*, 1910, **151**, 817—819. Compare this vol., i, 301).—Further experimental details are given for the preparation of starch free from electrolytes by the method previously described. Potato starch is the variety most amenable to this method of purification. The material so obtained contains less than 0·02% of ash. With hot water it gives a colloidal solution less viscous than an ordinary starch solution, but from which the substance is precipitated by dilution. W. O. W.

The Adsorption of Acids by Carbohydrates. FRED. ROBINSON (*Proc. Camb. Phil. Soc.*, 1910, **15**, 548—558. Compare Fenton and Gostling, Trans., 1898, **73**, 554).—The dry carbohydrate is covered with chloroform or carbon tetrachloride, a standard solution of dry hydrogen chloride or bromide in the same solvent is then added, and, after several hours, a known volume is withdrawn, shaken with water, and titrated with barium hydroxide.

Carbohydrates adsorb the acids rapidly, the results agreeing well with an exponential adsorption formula, but the relative order of adsorption is not related to the chemical nature of the carbohydrate. It is also independent of chemical action, as the adsorptive power of starch is the greatest, although starch yields the smallest quantity of chloromethylfurfuraldehyde. Lactose and dextrose have the lowest adsorptive power, lactose and maltose differing widely. Lævulose and sucrose become pink, and finally black, with hydrogen bromide. C. H. D.

Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1910, **23**, 2030—2031).—The conclusions of Jentgen (this vol., i, 654) are erroneous, as the cellulose used would retain a considerable quantity of

* and *J. Pharm. Chim.*, 1910, [vii], **2**, 481—490.

water, so that the acid is diluted with water, and is not in the so-called molecular condition. C. H. D.

Nitrous Esters of Cellulose. PAUL NICOLARDOT and GEORGES CHERTIER (*Compt. reud.*, 1910, **151**, 719—722).—Estimation of the nitrogen in nitrated cellulose by the Schlœsing method always gives a higher result than when the analysis is effected in the Lunge nitrometer. This appears to be due to the existence of nitrous esters, which undergo immediate decomposition when dissolved in sulphuric acid. Attempts to prepare such compounds by the action of oxides of nitrogen on cotton under various conditions were unsuccessful, oxidation usually taking place. By their action on viscose, however, in presence of acetic acid, a product was obtained containing 3% of nitrogen (Schlœsing) or 5% (Lunge). This was freed from nitrates by treatment with acetone, in which the nitrites are insoluble.

The nitrous esters of cellulose are somewhat unstable, grey substances, pulverulent when dry, but gelatinous when wet. They are insoluble in water and organic solvents; alkalis bring about hydrolysis, nitrites being formed. Hydrolysis is slowly effected by water at the ordinary temperature, and in contact with alcohols, decomposition occurs, the corresponding aldehyde or acid being produced. The deterioration of nitrated cotton is probably connected with the presence of these substances. W. O. W.

Ammonium and Oxonium Perchlorates. Relationship between Constitution and Behaviour towards Water. KARL A. HOFMANN, R. ROTH, K. HÖBOLD, and A. METZLER (*Ber.*, 1910, **43**, 2624—2630. Compare this vol., i, 105, 168, 187, 370).—The solution of perchlorates in water is primarily due to the formation of hydrates; electrolytic dissociation and hydrolysis are secondary phenomena. Quaternary ammonium perchlorates are not so readily soluble in water as the perchlorates derived from primary, secondary, and tertiary amines. Diazonium perchlorates and the perchlorates of the magenta and methylene-blue series are also sparingly soluble.

Oxonium perchlorates of the type $R_2O,HClO_4$ are readily soluble, whereas tertiary perchlorates, $R_3O\cdot ClO_4$, are sparingly soluble.

These phenomena are attributed to subsidiary valencies of the acidic H atom, which can be used up in attaching water to the molecule of the acid or salt.

The following salts are described: *Trimethylammonium perchlorate*, $NHMe_3\cdot ClO_4$, doubly refracting prisms and pyramids; at 17°, 20 grams dissolve in 100 of water; *trimethylamineoxide perchlorate*, $NMe_3O,HClO_4$, hygroscopic cubes; *ethylenediamine perchlorate*, $C_2H_8N_2,2HClO_4$, compact prisms, soluble in its own weight of water at 17°; *tetramethylammonium perchlorate*, $NMe_4\cdot ClO_4$, tetragonal crystals, decomposing above 300°, solubility 0·341 at 12°, 1·008 at 19°, and 1·554 at 25°; *tetraethylammonium perchlorate*, solubility 2·392 at 17°, decomposes above 300°; *trimethylethylammonium perchlorate*, long, rectangular prisms, solubility 11·06 at 17° and 11·97 at 20°; *trimethylbromoethyl perchlorate*, $C_2H_4Br\cdot NMe_3\cdot ClO_4$, rectangular plates, m. p. about 200° (decomp.), solubility 3·59 at 19°; *choline perchlorate*, $OH\cdot C_2H_4\cdot NMe_3\cdot ClO_4$, glistening, rectangular plates from absolute

alcohol, solubility 0·89 at 20°; *neurine perchlorate*, $C_2H_3 \cdot NMe_3 \cdot ClO_4$, short prisms, solubility 5·764 at 0°, also soluble in 30% hydrogen peroxide; *betaine perchlorate*, $C_2H_3O_2 \cdot NMe_3 \cdot ClO_4$, doubly refractive plates, solubility 17·73 at 19°; *diphenyliodonium perchlorate*, $IPh_2 \cdot ClO_4$, colourless, felted needles, solubility 0·624 at 19·6°. The perchlorates of malachite-green, crystal-violet, and methylene-blue are so sparingly soluble that the solubilities can be estimated by the colorimetric method only. The perchlorates of the corresponding leuco-bases are much more readily soluble. *Magenta tetraperchlorate*, $C_9H_{17}N_3,4HClO_4$, is a dark orange-coloured, crystalline powder, obtained by mixing the monoperchlorate with 60% perchloric acid solution and ether; it decomposes above 300° and is hydrolysed by water to the monoperchlorate. *p*-Phenylenediamine, *p*-phenylenedimethyldiamine, acetyl-*p*-phenylenediamine, and *m*-phenylenediamine, all yield sparingly soluble crystalline diazonium perchlorates, that derived from *p*-phenylenediamine being extremely explosive. The diazo-compounds from *o*-phenylenediamine and *o*- and *p*-aminophenol do not yield crystalline perchlorates.

The following alkaloid perchlorates are formed as precipitates when acetic acid solutions of the base are mixed with excess of 20% perchloric acid solution: Cinchonine perchlorate (2), prisms; *strychnine perchlorate* (1), long needles, solubility 0·22 at 15°; *brucine perchlorate* (1), rhombic plates, solubility in 2% perchloric acid solution 0·15 at 18°; *morphine perchlorate* (1), glistening needles, solubility in 4% acid 0·44 at 15°; *cocaine perchlorate* (1), long needles, solubility in 8% acid 0·26 at 6°. The numbers refer to the number of molecules of acid combined with one molecule of alkaloid. Quinine, quinidine, kairine, thalline, nicotine, piperidine, piperazine, and solanine are not precipitated by 20% perchloric acid.

Anisaldehyde perchlorate, $2OMe \cdot C_6H_4 \cdot CHO,HClO_4$, crystallises from ethereal solution in colourless prisms or plates, which deliquesce in contact with the air. *Chrysoquinone perchlorate*, $C_{18}H_{10}O_2,HClO_4$, forms dark violet-coloured prisms, decomposing at about 190°. Anthranol, anthraquinone, diphenylene oxide, and phenyl ether do not yield perchlorates, but dibromophenyl ether and dibromodiphenylene-oxide yield sparingly soluble perchlorates (3 mols. of oxygen compound to 1 of acid) which are hydrolysed by water.

Xanthoxonium perchlorate, $C_{13}H_9O \cdot ClO_4$, prepared from an ethereal solution of xanthhydrol and 70% perchloric acid, forms intensely yellow crystals; these decompose at 235°, and are hydrolysed by water to xanthhydrol and perchloric acid, but are more stable than the crystals of xanthone perchlorate. The group $X \cdot O \leqslant$ is thus comparatively stable (compare Baeyer, this vol., i, 763). J. J. S.

Some Derivatives of Pentamethylenediamine and a New Convenient Synthesis of 2-Methylpyrrolidine from Piperidine. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 2864—2879).—2-Methylpyrrolidine, which cannot be obtained from piperidine in the same way that 2-methyldihydroindole is prepared from tetrahydroquinoline, has been synthesised as follows: Benzoylpiperidine is converted by phosphorus

pentachloride into benzoyl-ε-chloroamylamine, and this, for practical purposes, is changed by excess of alcoholic sodium iodide into benzoyl-ε-iodoamylamine. The latter reacts rapidly with warm alcoholic 33% trimethylamine to form *ε-benzoylaminotrimethylamylammonium iodide*, $NHBz\cdot[CH_2]_5\cdot NMe_3I$, m. p. 189°. (The corresponding chloride is an oil which yields a *platinichloride*, m. p. 198°.) The iodide is converted in the usual manner into a solution of the hydroxide, which, after evaporation to dryness, yields by distillation in a vacuum a mixture of *benzoyldimethylpentamethylenediamine*, $NHBz\cdot[CH_2]_5\cdot NMe_2$, b. p. 220—225°/10 mm. (*picrate*, oily; methiodide, m. p. 189°, as above), and *pentenylbenzamide*, $CH_2{:}CH\cdot[CH_2]_3\cdot NHBz$, b. p. 195°/13 mm., which is easily separated, owing to the insolubility of the latter in dilute acids. The solution of the unsaturated compound in concentrated hydrochloric acid, after many hours at 70°, yields on cooling impure benzoyl-δ-chloroamylamine, which is converted by concentrated hydrochloric acid at 150—160° into *δ-chloroamylamine hydrochloride*; this forms a *platinichloride*, m. p. 192°, and is converted into 2-methylpyrrolidine by warming with alkalis. Since the m.p.'s of the platinichloride and of the aurichloride, 181—192° (decomp.) and 184° respectively, of the 2-methylpyrrolidine thus prepared do not agree with those, 206—207° (decomp.) and 158—161° respectively, of Tafel and Fenner's 2-methylpyrrolidine, the author's base has been converted by exhaustive methylation into the quaternary methiodide, the platinichloride of which, decomp. 255°, blackening at 240°, agrees exactly with the corresponding derivative of Tafel and Fenner's base.

Benzoyldimethylpentamethylenediamine can be readily prepared by heating aqueous dimethylamine (2 mols.) and benzoyl-ε-chloroamylamine on the water-bath. By hydrolysis with hydrochloric acid at 150° it yields as-*dimethylpentamethylenediamine*, $NMe_2\cdot[CH_2]_5\cdot NH_2$, b. p. 181—182° (*aurichloride*, m. p. 168°). *Benzoyldiethylpentamethylenediamine*, $NEt_2\cdot[CH_2]_5\cdot NHBz$, b. p. 232—234°/10 mm., similarly prepared from diethylamine, yields by hydrolysis as-*diethylpentamethylenediamine*, b. p. 87—88°/10 mm. [*platinichloride*, m. p. 215° (decomp.); *picrate*, m. p. 110°]. *Benzoyldi*iso*butylpentamethylenediamine*, $NHBz\cdot[CH_2]_5\cdot N(C_4H_9)_2$, b. p. 250°/10 mm. (decomp.), yields by hydrolysis as-*di*iso*butylpentamethylenediamine*, b. p. 126—127°/11 mm. (*platinichloride*, m. p. 212°). These three *as*-dialkylpentamethylenediamines are almost odourless, remain unchanged above 200°, are almost unaffected by air, and do not react with nitrous acid. This inactivity is attributed to steric causes, not to a concentration of the basic properties at the tertiary nitrogen atom to such an extent that the primary nitrogen atom no longer exerts basic functions. The latter explanation is rejected because as-*phenylmethylpentamethylenediamine*, $NH_2\cdot[CH_2]_5\cdot NPhMe$, b. p. 180°/16 mm. (prepared by hydrolysing the benzoyl derivative obtained from methylaniline and benzoyl-ε-iodoamylamine), in which the tertiary nitrogen atom probably has a weaker basic function than the primary, reacts with nitrous acid without the evolution of a gas (probably, therefore, a nitroso-group enters the phenyl nucleus), and also because o-γ-*dimethylaminopropylaniline*, $NMe_2\cdot[CH_2]_3\cdot C_6H_4\cdot NH_2$, b. p. 151°/15 mm. [*picrate*, m. p. 173—174°; *platinichloride*, m. p. 213° (decomp.)], in which the aromatic amino-

group is certainly weaker than the aliphatic dimethylamino-group, reacts with nitrous acid with evolution of nitrogen, forming a substance which is soluble in alkalis and is therefore probably o-γ-dimethylaminopropylphenol. o-γ-Dimethylaminopropylaniline is obtained by hydrolysing its benzoyl derivative, which is prepared from o-γ-chloropropylbenzanilide and dimethylamine.

Di-ϵ benzoylaminodimethylamyl ammonium iodide,

$$(NHBz\cdot[CH_2]_5)_2NMe_2I,$$

m. p. 162°, obtained as a by-product in the reaction between dimethylamine and benzoyl-ϵ-iodoamylamine, is converted by hydriodic acid at 160° into *di-ϵ-aminodimethylamylammonium iodide dihydriodide*, $(HI,NH_2\cdot[CH_2]_5)_2NMe_2I$, m. p. 210°; the corresponding *dihydrochloride*, $(HCl,NH_2\cdot[CH_2]_5)_2NMe_2Cl$, has m. p. 240°, and forms a *platinichloride*, m. p. 221°. The dihydriodide by exhaustive methylation yields the tris-quaternary *ammonium iodide*,

$$NMe_3I\cdot[CH_2]_5\cdot NMe_2I\cdot[CH_2]_5\cdot NMe_3I,$$

which does not melt at 300°; the corresponding tris-quaternary *chloride* is extremely hygroscopic, and forms a *platinichloride*, m. p. 260°, blackening at about 250°. C. S.

Cyclic Imines. IV. Constitution of Hexamethyleneimine and the Action of $\alpha\zeta$-Di-iodohexane on Bases. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 2853—2864).—The presence of a seven-membered heterocyclic ring in hexamethyleneimine, which is denied by Blaise and Houillon (Abstr., 1906, i, 692), is proved by distilling *benzoylhexamethyleneimine*, b. p. 206—208°/19 mm., with phosphorus pentachloride and boiling the portion of the distillate which is insoluble in water with an excess of alcoholic sodium phenoxide for ten hours, whereby $\alpha\zeta$-diphenoxyhexane is obtained in 65% yield.

The reactions between $\alpha\zeta$-di-iodohexane and methylamine, dimethylamine, aniline, and piperidine do not yield a trace of hexamethyleneimine derivatives, the products being derivatives of $\alpha\zeta$-diaminohexane and of α-pipecoline, and substances of high molecular weight. Thus $\alpha\zeta$ di-iodohexane and aqueous methylamine (4 mols.) in the presence of a little alcohol, after two days at the ordinary temperature, yield 10% of 1-methyl-2-pipecoline (identified in the form of the methiodide, m. p. 255°, and the platinichloride, decomp. 222°, obtained therefrom), 13% of dimethyl-$\alpha\zeta$-diaminohexane (*dibenzenesulphonyl* derivative, m. p. 182°; *picrate*, m. p. 137°), and about 70% of a mixture of substances of high molecular weight. When heated on the water-bath for many hours, $\alpha\zeta$-di-iodohexane and aniline (3 to 4 mols.) yield, not phenylhexamethyleneimine or phenyl-α-pipecoline, but about 50% of *diphenyl-$\alpha\zeta$-diaminohexane*, $NHPh\cdot[CH_2]_6\cdot NHPh$, m. p. 74°, which forms a *picrate*, m. p. 172°, a *dibenzoyl* derivative, m. p. 163°, and a *dinitroso*-compound, m. p. 69°. $\alpha\zeta$-Di-icdohexane and dimethylamine yield dimethyl-2-pipecolinium iodide and *tetramethyl-$\alpha\zeta$-diaminohexane*, $NMe_2\cdot[CH_2]_6\cdot NMe_2$, b. p. 103°/20 mm., which forms a *picrate*, m. p. 162°, and a *methiodide*, which does not melt at 270°. $\alpha\zeta$-Di-iodohexane and piperidine in alcoholic solution on the water-bath yield about 50% of *$\alpha\zeta$-di-1-piperidylhexane*,

$$C_5NH_{10}\cdot[CH_2]_6\cdot C_5NH_{10},$$

b. p. 198°/16 mm. (*picrate*, m. p. 208°, blackening at 195°; *platinichloride*, m. p. 230°; *methiodide*, m. p. 240°), together with a quaternary *iodide*, $CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}>NI<\begin{smallmatrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{smallmatrix}>CH_2$, m. p. 263°, which is identical with the product obtained from 2-pipecoline and $\alpha\epsilon$-di-iodopentane.

The preceding behaviour of di-iodohexane with primary and secondary bases proves that caution is necessary in assigning cyclic structures to substances produced in reactions in which the reagents employed would, apparently obviously, produce ring compounds.

C. S.

Detection of Choline. Trimethylamine. MAX KAUFFMANN and DANIEL VORLÄNDER (*Ber.*, 1910, **43**, 2735—2743).—Choline platinichloride is dimorphous; it separates from water in monoclinic anhydrous crystals, and from dilute alcohol in regular octahedra and cubes or combinations of these. The monoclinic salt is slightly deeper orange in colour; both have m. p. 215—240° with frothing. The monoclinic salt is doubly refractive. The conversion of one form into the other takes place on crystallisation from water or 50% alcohol respectively, and affords a certain test for the presence of choline. Choline may also be detected by distillation with potassium hydroxide, when trimethylamine is formed and recognised by its odour. When trimethylamine is smelt for any length of time, the odour becomes firstly like that of a monoamine, and subsequently like that of ammonia which persists. Many other substances show a similar "reversal of odour."

When choline chloride is heated with excess of benzenesulphonyl chloride, trimethylchloroethylammonium chloride, $NMe_3(C_2H_4Cl)Cl$, is formed. The platinichloride crystallises in octahedra, m. p. 251°; the *aurichloride* forms slender, yellow, doubly-refractive needles. This chloroethyl base takes a middle position between neurine and choline in its toxic qualities.

By the interaction of aqueous trimethylamine and benzenesulphonyl chloride, a quaternary ammonium salt is obtained. The *platinichloride*, $(SO_2Ph\cdot NMe_3)_2PtCl_6,4H_2O$ (?), crystallises in anisotropic, prismatic, or tabular forms, m. p. 209—223°. The *aurichloride* separates in microscopic, doubly-refractive needles, m. p. 196°, decomp. 246°. The *chloride* was obtained in needles; it gives a yellow precipitate with picric acid.

E. F. A.

Derivatives of Amino-alcohols. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1910, [vii], 2, 337—344, 397—401. Compare this vol., i, 246).—The first paper deals with the esterification of these alcohols, and shows (1) that the salts of such esters are easily crystallisable, and are convenient for the identification of the alcohols; (2) that they are readily obtained by mixing solutions in benzene of the amino-alcohols and the necessary acid chloride or bromide, and (3) that this method of formation appears to be analogous with Einhorn's method of using pyridine to promote esterification of alcohols, an additive product of the type $CH_2R\cdot N(CO\cdot R)R_2Cl$ being formed in both cases, which on

warming yields the ester. Maire's observation that amino-alcohols containing two ethyl groups attached to the nitrogen atom behave abnormally, is confirmed (Abstr., 1908, i, 248), but an ester was obtained in this case by avoiding the use of any solvent. Such amino-alcohols, however, behave normally with cinnamoyl chloride. The esters of the amino-alcohols are liquid, distil without decomposition, are stable towards alkalis, are easily hydrolysed by mineral acids, and are much less basic than the amino-alcohols; they have little or no odour. Their halogen acid salts crystallise well as a rule, but may be hygroscopic. The second paper describes a series of amides obtained by the application of the Schotten-Baumann reaction to the amino-alcohols. In these conditions no esterification of the hydroxyl group occurs.

Dimethylaminotrimethylcarbinol hydrochloride furnishes a *benzoate*, m. p. 202°, crystallising with 1 mol. of alcohol, a *cinnamate*, m. p. 208°, and an iso*valerate*, m. p. 125°. Dimethylaminodimethylethylcarbinol gives a *benzoate*, b. p. 150°/13 mm., a *diethylcarbamate*,

$$NMe_2 \cdot CH_2 \cdot CMeEt \cdot O \cdot CO \cdot NEt_2,$$

b. p. 136°/41 mm. [the *hydrochloride* of which, m. p. 142° (decomp.), crystallises from acetone in hygroscopic needles, and yields an *aurichloride*, m. p. 98°, which forms orange-red needles, whilst the *hydrobromide*, m. p. 148°, is very soluble in alcohol and exhibits a marked sedative action], a *valerate*, b. p. 128°/23 mm. (yielding a *hydrochloride*, m. p. 151°, and a *hydrobromide*, m. p. 126°, both of which are anæsthetics), a *bromovalerate hydrochloride*, m. p. 158°, which is markedly anæsthetic, a *diethylacetate hydrobromide*, m. p. 169°, a *bromodiethylacetate hydrochloride*, m. p. 160°, a *hexoate*, b. p. 152° (under reduced pressure), a *bromohexoate hydrochloride*, m. p. 130°, a *bromoheptoate hydrochloride*, m. p. 128° (which is markedly anæsthetic), and a *bromolaurate hydrochloride*, m. p. 99°. The higher homologues beyond the hexoate show increasingly the characters of the acid group, and exhibit the properties of soaps. The *hydrochlorides* of the *benzoyl* derivatives of the following amino-alcohols: dimethylaminomethyldiethylcarbinol, dimethylaminodimethylpropylcarbinol, diethylaminodimethylethylcarbinol, and dimethylaminodimethyl*iso*amylcarbinol melt at 180°, 146°, 140°, and 142° respectively. The last of these gives a *platinichloride*, m. p. 178°, and the amino-alcohol also furnishes a *cinnamate hydrochloride*, m. p. 110°.

Aminodimethylethylcarbinol gives with bromovaleryl chloride an *amide*, $CHMe_2 \cdot CHBr \cdot CO \cdot NH \cdot CH_2 \cdot CMeEt \cdot OH$, m. p. 93°, forming brilliant octahedral crystals. Valeryl chloride yields with the same amino-alcohol an *amide*, m. p. 50—60°, b. p. 190°/32 mm., and with methylaminodimethylethylcarbinol and iminobisdimethylethylcarbinol, *amides*, having b. p. 163°/25 mm. and 210°/23 mm. respectively; the second substance crystallises in spangles, and has m. p. 152—153°. All these amides are sedative, and some of them hypnotic; they are less toxic than the corresponding esters described in the first paper.

Ethyl chlorocarbonate reacts in presence of sodium hydrogen carbonate with aminodimethylethylcarbinol to form the *urethane*, $OH \cdot CMeEt \cdot CH_2 \cdot NH \cdot CO_2Et$, b. p. 151—152°/17 mm., whilst with

the same alcohol propyl chlorocarbonate furnishes the *propyl* ester, having b. p. 174—175°. These urethanes are hypnotic in action, but must be given in large doses, for example, 0·4 gram per kilo. of body weight in rabbits. They are toxic to rabbits in doses of 1·8 grams per kilo.

Aminodimethylethylcarbinol with potassium *iso*cyanate yields the substituted *carbamide*, $OH{\cdot}CMeEt{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 150°, which is a powerful hypnotic; the corresponding *methylcarbamide*, similarly obtained, has m. p. 128°, and *carbamide bisdimethylethylcarbinol*, m. p. 90° (approx.). T. A. H.

Carnitine; Synthesis of γ-Trimethylamino-β-hydroxybutyric Acid. R. Engeland (*Ber.*, 1910, **43**, 2705—2707).—Carnitine, present in meat extract, has been pronounced to be γ-trimethylamino-α-hydroxybutyric acid (Engeland, Abstr., 1909, i, 557). It is shown now to differ from γ-trimethylamino-β-hydroxybutyric acid, which is obtained synthetically by heating epichlorohydrin with anhydrous hydrogen cyanide to form chlorohydroxybutyronitrile; this, when heated with alcoholic trimethylamine in sealed tubes at 110°, or even in open vessels at 70—80°, is converted into the *chloride* of *γ-trimethylamino-β-hydroxybutyronitrile*. The *aurichloride* of this compound crystallises in reddish-yellow prisms, m. p. 124—125°. Hydrolysis of the nitrile requires ten hours' boiling with a mixture of aqueous and alcoholic hydrochloric acid. A by-product is a bimolecular anhydride-like product, of which the sparingly soluble *aurichloride*, $C_{14}H_{30}O_5N_2,2AuCl_4$, was analysed. The *aurichloride* of *γ-trimethylamino-β-hydroxybutyric acid* crystallises in reddish-yellow plates, m. p. 145°, decomp. at 225°. The *chloride* crystallises in needles, sparingly soluble in alcohol. When heated with alcohol containing hydrogen chloride, it is converted quantitatively into the *ethyl* ester, the *platinichloride* of which sinters at 200°, m. p. 210—212°. These derivatives are very different from those of carnitine.

E. F. A.

Syntheses of Hydroxybetaines. II. Synthesis of γ-Trimethyl-β-hydroxybutyrobetaine (*dl*-*iso*Carnitine). Adolf Rollett (*Zeitsch. physiol. Chem.*, 1910, **69**, 60—65. Compare this vol., i, 658).—*Ethyl γ-trimethylamino-β-hydroxybutyrate chloride*, $NMe_3Cl{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et$, is formed when Lespieau's ethyl γ-chloro-β-hydroxybutyrate (Abstr., 1899, i, 243, 790) is heated with an alcoholic solution of trimethylamine for six hours at 100°. The *platinichloride*, $C_{18}H_{40}O_6N_2PtCl_6$, crystallises from 90% alcohol in slender, pale yellow needles, which decompose at 233—234°. The *platinichloride* of the corresponding acid,

$$[NMe_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H]_2PtCl_6,$$

forms orange-coloured crystals, decomposing at 248°, and is isomeric with carnitine platinichloride (m. p. 214—218°).

A by-product obtained in the preparation of the ester is trimethylethylammonium chloride, which is deposited as the *platinichloride*, $(NMe_3Et)_2PtCl_6$, in the form of pale orange-coloured plates decomposing at 281—284°. The corresponding *aurichloride*, $NMe_3EtCl,AuCl_3$, forms characteristic needles, which are unchanged at 290°. J. J. S.

Action of Ammonia on Unsaturated Acids. II. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 885—890. Compare Abstr., 1909, i, 772).—In order to confirm the explanation already given for the formation of imino-acids by the action of aqueous ammonia on unsaturated acids, a mixture of crotonic and aminoacetic acids was heated in a sealed tube at 120—130° with sufficient aqueous ammonia to convert both acids into their ammonium salts. The products of the reaction were ethyl β-aminobutyrate and *diethyl-β-iminobutyrateacetate*, $CO_2Et\cdot CH_2\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2Et$, b. p. 144°/19 mm., D_4^{20} 1·0340, n_D^{20} 1·4370, a colourless, mobile liquid, soluble in alcohol and ether, and readily saponified into β-iminoacetic-butyric acid, $CO_2H\cdot CH_2\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2H$, m. p. 200° (decomp.). To avoid the formation of β-amino-acid, and thus make this a convenient general method for the preparation of imino-acids, the ammonium salts are substituted by the potassium salts of the amino- and unsaturated acids. To prove that glycine unites with crotonic acid in the β-position, propaldehyde and potassium cyanide were made to react with the hydrochloride of ethyl aminoacetate, when *α-iminoacetic-butyric acid*, $CO_2H\cdot CHEt\cdot NH\cdot CH_2\cdot CO_2H,H_2O$, was formed. It forms large, elongated prisms, m. p. 104—105°. The *hydrochloride* forms small crystals, decomposing at 175—177°.

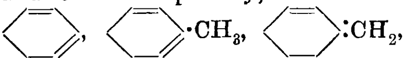
Thus, in the interaction of α-amino-acids with crotonic acid, $\alpha\beta$-imino-dialiphatic acids are formed. Z. K.

Synthesis of γ-Guanidinobutyric Acid. R. ENGELAND and FR. KUTSCHER (*Ber.*, 1910, **43**, 2882—2883).—This substance may be readily prepared by the following method. Concentrated solutions of cyanamide and of twice its weight of γ-aminobutyric acid are mixed, rendered alkaline with a few drops of ammonia, and kept for five weeks at the ordinary temperature, the evaporated ammonia being replaced from time to time. The guanidinobutyric acid which crystallises out is purified by conversion into the hydrochloride, which is sparingly soluble in concentrated hydrochloric acid and in alcohol. The *aurichloride*, $C_5H_{12}O_2N_3AuCl_4$, forms broad, lustrous plates, m. p. 198—200°. The *hydrochloride* regenerated from it has m. p. 184°; it is precipitated by phosphotungstic acid even from dilute solutions, but not by picric acid or sodium picrate. The synthetic acid is identical with that obtained by oxidation of arginine or agmatine.

R. V. S.

Action of Some Salts of Tervalent Metals on Thiocyanates. CORRADO BONGIOVANNI (*Boll. chim. farm.*, 1910, **49**, 789—791. Compare Abstr., 1908, i, 859).—Molybdenum thiocyanate is decolorised by the same substances which decolorise ferric thiocyanate. Chromic hydroxide and thiocyanic acid yield a reddish-violet solution, which is much less intensely coloured than that of ferric thiocyanate, and it behaves differently in other respects, for it is not hydrolysed appreciably, and is not decolorised by saline solutions, oxalic acid, or acetic acid. Vanadium thiocyanate behaves similarly to the ferric compound. The mode of formation and the properties of these substances do not accord with Tarugi's hypothesis (*loc. cit.*) as to their constitution. R. V. S.

Orientation in the Benzene Nucleus. JULIUS OBERMILLER (*J. pr. Chem.*, 1910, [ii], **82**, 462—472).—A reply to, and a claim for priority over, Holleman. C. S.

Unsaturated Hydroaromatic Hydrocarbons with Semicyclic Double Linkings. KARL AUWERS and G. PETERS (*Ber.*, 1910, **43**, 3076—3094).—In two papers published already (this vol., ii, 365, 367), Auwers and Eisenlöhr discuss the determination of constitution by optical methods, and point out the importance of ascertaining the normal value of the exaltation of refractivity and dispersivity in undisturbed conjugated systems and the influence thereon of various kinds of distortion. In pursuance of this object they are attempting to prepare and examine optically, substances derived from the three systems  and the present paper gives the results of attempts to solve this question for the third of these

1 : 3-Dimethyl-Δ^3-*cyclo*hexen-5-one on treatment with magnesium methyl iodide furnishes 1 : 3 : 5 - *trimethyl*-Δ^3-cyclo*hexen*-5-*ol*, m. p. 46°, b. p. 87—90°/17 mm., D_4^{20} 0·9132 to 0·9140, $n_D^{19 \cdot 3}$ 1·47349, $n_\alpha^{19 \cdot 3}$ 1·47053, and $n_\gamma^{19 \cdot 3}$ 1·48715 (whence $\Sigma_\alpha = +0{\cdot}36$, Σ_D $+0{\cdot}34$, and $\Sigma_\gamma - \Sigma_\alpha + 9\%$) ; it is crystalline. On heating alone or with dehydrating agents, it yields a hydrocarbon having b. p. 63—64°/17 mm. or 151°/760 mm., D_4^{20} 0·821 to 0·828, n_α^{20} 1·467 to 1·477, n_D^{20} 1·471 to 1·481 (whence $\Sigma_\alpha = +0{\cdot}68$ to $+1{\cdot}02$, and $\Sigma_\gamma - \Sigma_\alpha$ varies from 24 to 40%). These data agree with the assumption that the hydrocarbon is 1 : 3 - *dimethyl*-5 - *methylene* - Δ^3 - cyclo*hexene*, $CH_2<\begin{matrix}CMe=CH\\CHMe\cdot CH_2\end{matrix}>C{:}CH_2$, and belongs to the third system referred to above. On oxidation with permanganate, it furnishes a saturated neutral *substance*, $C_9H_{16}O_3$, m. p. 96—97°, but on treatment with ozone in acetic acid it yields γ-acetyl-β-methylbutyric acid (Knoevenagel and Brunswig, Abstr., 1902, i, 640), identical with that obtained by the action of permanganate or ozone on 1 : 3 - dimethyl - Δ^3 - *cyclo*hexen-5-one, which is probably formed as an intermediate product in the oxidation of the hydrocarbon. γ-Acetyl-β-methylbutyric acid has b. p. 140—142°/12 mm., $D_4^{18 \cdot 7}$ 1·0614, $n_\alpha^{18 \cdot 2}$ 1·44383, $n_D^{18 \cdot 2}$ 1·44611, and yields a crystalline *semicarbazone*, m. p. 170—171°. The hydrocarbon on bromination and subsequent treatment with potassium hydroxide in alcohol yields mesitylene.

1 : 3-*Dimethyl*-5-*ethylidene*-Δ^3-cyclo*hexene*, b. p. 178°, D_4^{20} 0·833 to 0·837, n_α^{20} 1·476 to 1·483, n_D^{20} 1·480 to 1·487 (whence $\Sigma_\alpha = +0{\cdot}80$ to $+1{\cdot}05$, $\Sigma_D + 0{\cdot}84$ to $+1{\cdot}10$, and $\Sigma_\gamma - \Sigma_\alpha = +27$ to 40%), probably identical with Klages' dihydroethylxylene (Abstr., 1907, i, 597), is obtained by heating the corresponding tertiary alcohol alone or with oxalic acid.

1 : 3-*Dimethyl*-5-iso*propylidene*-Δ^3-cyclo*hexene*, similarly prepared, has b. p. 101°/36 mm. or 196°/760 mm., D_4^{20} 0·841 to 0·848, n_α^{20} 1·481 to 1·492, n_D^{20} 1·485 to 1·496 (whence $\Sigma_\alpha = +0{\cdot}70$ to $+1{\cdot}20$, $\Sigma_D = +0{\cdot}73$ to $+1{\cdot}26$, and $\Sigma_\gamma - \Sigma_\alpha = 33$ to 51%). These hydrocarbons agree in general properties with the similar products containing semicyclic double linkings described by Wallach (Abstr., 1907, i, 425), but possibly all of them contained isomerides having two *endo*cyclic double linkings.

Pure hydrocarbons of this type probably have $\Sigma_\alpha = +1{\cdot}0$ to $1{\cdot}2$, $\Sigma_D = +1{\cdot}1$ to $1{\cdot}3$, and $\Sigma_\gamma - \Sigma_\alpha = 40$ to 50%. T. A. H.

Reducibility of Conjugated Double Linkings in Hydroaromatic Substances. KARL AUWERS and G. PETERS (*Ber.*, 1910, **43**, 3111—3120).—An extension of the work described in the preceding abstract and this vol., i, 841. The results resemble those obtained by Klages (Abstr., 1904, i, 45, 1001) in the case of styrene derivatives, and show that the reducibility of the hydroaromatic hydrocarbons depends on the number, nature, and distribution of the side-chains attached to the carbon atoms in the double linkings of the conjugated system. This influence has been illustrated already by the reduction of 3-chloro-*iso*terpinolene to a mixture of menthenes (this vol., i, 122), by Semmler's reduction of chlorocarvenene to the corresponding hexadiene under similar conditions, and by the non-reducibility of hydrocarbons of this type, described by Rupe and Emmerich (Abstr., 1908, i, 556).

5-Chloro-1 : 3-dimethyl-$\Delta^{3:5}$-*cyclo*hexadiene, already prepared by Klages and Knoevenagel (Abstr., 1895, i, 654), has b. p. 68—70°/17 mm., $D_4^{15\cdot4}$ 1·0065, n_α 1·50022, n_D 1·50459 (whence $\Sigma_D = +0{\cdot}69$), but the sample was probably not quite pure. On careful reduction with sodium in wet ether it yielded 1 : 3-dimethyl-$\Delta^{3:5}$-*cyclo*hexadiene, b. p. 128—129°/760 mm., D_4^{20} 0·821, n_α^{20} 1·467, n_D^{20} 1·471 (whence $\Sigma_\alpha = +0{\cdot}62$, $\Sigma_D = +0{\cdot}68$, and $\Sigma_\gamma - \Sigma_\alpha = 26\%$), which furnished a *dihydrochloride*, b. p. 93—97°/16 mm., and is possibly identical with the dihydro-*m*-xylene described by Harries and Antoni (Abstr., 1903, i, 614), the difference in physical constants being perhaps due to impurity in both specimens. On further reduction in ether or, better, in alcohol, the chlorodimethyl*cyclo*hexadiene furnishes 1 : 3-dimethyl-Δ^4-*cyclo*hexene, b. p. 126—127°/760 mm., D_4^{20} 0·806, n_α^{20} 1·447, n_D^{20} 1·450 (whence $\Sigma_\alpha = +0{\cdot}26$, $\Sigma_D = +0{\cdot}24$, and $\Sigma_\gamma - \Sigma_\alpha = +9\%$) (compare Knoevenagel, Abstr, 1897, i, 606), which yields a *monohydrochloride*. T. A. H.

Derivatives of 1 : 3-Dichloro-4-iodobenzene with a Multivalent Iodine Atom. CONRAD WILLGERODT and MATHIAS BÖLLERT (*Ber.*, 1910, **43**, 2641—2646).—2 : 4-Dichloroaniline is best prepared by the action of concentrated hydrochloric acid and potassium chlorate on acetanilide and subsequent hydrolysis of the acetyl derivative by boiling with hydrochloric acid. A small amount of *s*-trichloroaniline is formed at the same time, but this is readily removed, as it is insoluble in hydrochloric acid. The dichloroaniline can be transformed into the corresponding 1 : 3-*dichloro-4-iodobenzene*, $C_6H_3Cl_2I$, by the Sandmeyer reaction. The iodo-derivative has b. p. 257° (corr.), and yields a *dichloride*, $C_6H_3Cl_2{\cdot}ICl_2$, in the form of pale yellow needles, which decompose at 107°. 1 : 3-*Dichloro-4-iodosobenzene*, $C_6H_3Cl_2{\cdot}IO$, is a yellow-coloured powder with the characteristic iodoso-odour, and decomposes at about 196°. It does not yield stable salts. The *chromate* forms a red powder. *Di-m-dichlorophenyl-iodonium hydroxide*, $(C_6H_3Cl_2)_2I{\cdot}OH$, yields a faintly alkaline aqueous solution; the *iodide*, $(C_6H_3Cl)_2I{\cdot}I$, forms a yellow, crystalline precipitate, which decomposes at 135°; the *bromide* decomposes at 169°; the *chloride*, $(C_6H_3Cl_2)_2I{\cdot}Cl$,

is more readily soluble, and decomposes at 185°; the *platinichloride*, $C_{24}H_{12}Cl_{14}I_2Pt$, forms red needles, decomposing at 166°; the *mercurichloride*, $C_{12}H_6Cl_7IHg$, crystallises from alcohol in needles, m. p. 164° (decomp.), and the *dichromate*, $C_{24}H_{12}O_7Cl_8I_2Cr_2$, forms an orange-coloured precipitate, which is very unstable and explodes at 150°.

o-*Tolyl*-1 : 3-*dichlorophenyliodoniumiodide*, $C_6H_4Me{\cdot}I(C_6H_3Cl_2){\cdot}I$, prepared by Meyer and Hartmann's method (Abstr., 1894, i, 242) by shaking equivalent quantities of *o*-iodotoluene and 1 : 3-dichloro-4-iodosobenzene with freshly precipitated silver oxide and water and reducing with sulphur dioxide, is yellow, and has m. p. 127°. The *hydroxide* is soluble in water, yielding a faintly alkaline solution; the *chloride*, $C_{13}H_{10}Cl_3I$, is colourless, and has m. p. 203°; the *bromide*, $C_{13}H_{10}Cl_2BrI$, crystallises from ether in plates, sinters at 170°, and decomposes at 185°; the *nitrate*, $C_{13}H_{10}O_3NCl_2I$, has m. p. 183° (decomp.); the *dichromate*, $C_{26}H_{20}O_7Cl_4I_2Cr_2$, is yellow, and decomposes at 141°; the *mercurichloride*, $C_{13}H_{10}Cl_5IHg$, forms colourless needles, m. p. 163°.

Phenyl-1 : 3-*dichlorophenyliodonium iodide*, $C_6H_3Cl_2{\cdot}IPh{\cdot}I$, is yellow, but turns red on exposure to the air, and has m. p. 133°; the *chloride*, $C_{12}H_8Cl_3I$, crystallises in colourless needles, m. p. 203°; the *bromide* crystallises from alcohol in plates, m. p. 196°; the *platinichloride*, $C_{24}H_{16}Cl_{10}I_2Pt$, forms yellow needles, m. p. 156° (decomp.), and the *dichromate*, $C_{24}H_{16}O_7Cl_4I_2Cr_2$, has m. p. 146° (decomp.).

1 : 3-*Dichlorophenyl*-1 : 3-*dichloro*-4-*iodophenyliodonium chloride*, $C_6H_3Cl_2{\cdot}I(C_6H_2Cl_2I){\cdot}Cl$, crystallises from alcohol, and has m. p. 160°; the *bromide* crystallises in colourless needles, m. p. 131—132°; the *iodide*, $C_{12}H_5Cl_4I_3$, has m. p. 103°; the *dichromate*, $C_{24}H_{10}O_7Cl_8I_4Cr_2$, decomposes at 173°, and the *platinichloride*, $C_{24}H_{10}Cl_{14}I_4Pt$, forms a sparingly soluble, orange-coloured precipitate, m. p. 156°, after softening at 145°. J. J. S.

Limits of Activity of Chloromonoiodobenzenes with Regard to the Formation of Compounds with Multivalent Iodine. CONRAD WILLGERODT and KARL WILCKE (*Ber.*, 1910, **43**, 2746—2756). —s-*Trichlorophenyl iododichloride*, $C_6H_2Cl_3{\cdot}ICl_2$, crystallises in large, compact, sulphur-coloured leaflets, decomp. 100°.

s-*Trichloroiodosobenzene* is a slightly yellow, amorphous substance, which softens at 91°, decomp. 106°. The *basic sulphate*,

$$[C_6H_2Cl_3{\cdot}I(OH)]_2SO_4,$$

prepared by pouring 10% sulphuric acid on the iodoso-compound, is a colourless, crystalline powder, decomp. 168°. The *basic nitrate* is a bright yellow, crystalline mass, decomp. 143·4°, with evolution of red fumes. The *acetate* is obtained in colourless prisms grouped in rosettes, m. p. 166·8°.

s-Trichloroiodoxybenzene could not be obtained from the iodoso-compound.

Phenyl-s-*trichlorophenyliodinium chloride*, $C_6H_2Cl_3{\cdot}IPhCl$, is a yellow powder, m. p. 118—119°. The corresponding *iodide* begins to fuse at 90°, is melted clear at 140—150°, decomp. above 200°.

as-*Trichlorophenyl iododichloride* crystallises in small, sulphur coloured needles, decomp. 90°.

as-*Trichloroiodosobenzene* softens at 168°, decomp. 184°.

as-*Trichloroiodoxybenzene*, $C_6H_2Cl_3\cdot IO_2$, prepared by oxidation of the iodide chloride with sodium hypochlorite, forms needles, decomp. 240° without explosion.

as-Tetrachloroaniline has m. p. 89°. *as*-Tetrachloroiodobenzene does not form an iododichloride, and parts with iodine when chlorinated. Pentachloroaniline has m. p. 232°. On diazotisation and addition of potassium iodide, pentachloroiodobenzene is obtained in colourless crystals, m. p. 208·5°; it does not give an iododichloride.

It would seem that no iodoxy-compound is formed when iodine is situated between two halogen atoms; apparently these exercise a neutralising influence on the valency of the iodine atom, and prevent the attachment of the second oxygen atom. E. F. A.

Action of Nitric Acid on Saturated Hydrocarbons. IV. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 581—585. Compare Abstr., 1909, i, 372).—When saturated hydrocarbons are nitrated with nitric acid, it is found that with the diminution of the relative quantity of the latter, the nitration products increase, whilst the oxidation processes decrease. Now, aluminium nitrate, $Al(NO_3)_3,9H_2O$, melts at 73°, and decomposes completely into aluminium hydroxide and nitric acid at 140°, and between these two temperatures there is a certain equilibrium between the salt and its decomposition products. If, therefore, this salt is used for nitration, within these temperature limits the nitric acid will be used up as formed, and the equilibrium will thus be constantly disturbed. The acid will thus always be present in a relatively small quantity; the yield of nitration products should, therefore, be better than if an equivalent quantity of free nitric acid were employed. Experiments with *cyclo*hexane at 115—120° completely confirmed these considerations, a yield of 56·7% of mononitro-product being obtained; free nitric acid has never given such a high yield. *cyclo*Hexanone, possibly its nitro-derivative, $C_6H_{11}O_3N$, and *dinitrodi*cyclo*hexane*, $C_{12}H_{20}O_4N_2$, m. p. 216·5—217° (corr.), were formed as by-products. The latter, crystallising in small needles, was also obtained synthetically. Z. K.

***cyclo*Hexyl-ψ-nitrole.** S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 585—586).—When a few pieces of ice and then dilute sulphuric acid are added to a mixture of an alkaline solution of nitro-*cyclo*hexane and sodium nitrite, a blue oil at once separates, and collects at the bottom of the vessel. After some time, the oil is gradually converted into colourless crystals, which rise to the top of the liquid. These two substances are regarded as two modifications of the ψ-nitrole, the blue liquid being unimolecular, the solid, bimolecular.

Solid cyclo*hexyl-ψ-nitrole*, $C_6H_{10}O_3N_2$, m. p. 70—71° (decomp.), gives a blue solution in chloroform, and is oxidised by chromic acid in acetic acid solution, forming 1 : 1-*dinitro*cyclo*hexane*, b. p. 142—143°/35 mm., D_4^{21} 1·2452, n_D^{21} 1·4732, a heavy, yellow oil with a fairly pleasant odour. Z. K.

Action of Nitric Acid on Methyl*cyclo*hexane. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 691—701).—When methyl*cyclo*hexane is nitrated with nitric acid (D 1·2) or aluminium nitrate in a sealed tube, the chief product is the 1-nitro-derivative, the 3- and 4-nitro-derivatives also being obtained, more of the former when nitric acid is employed, and more of the latter with aluminium nitrate.

1-*Nitro*-1-*methyl*cyclo*hexane*, $C_7H_{13}O_2N$, b. p. 109—110°/40 mm., D_4^0 1·0547, D_4^{20} 1·0384, n_D^{20} 1·4580, is a colourless liquid with a pleasant odour; when heated with nitric acid, it is partly oxidised to succinic and oxalic acids, and with tin and hydrochloric acid it yields 1-amino-1-methyl*cyclo*hexane.

3-*Nitro*-1-*methyl*cyclo*hexane*, mixed with a very small quantity of the 1-nitro derivative, has b. p. 119—120°/40 mm., D_4^0 1·0547, D_4^{19} 1·0382, n_{19} 1·4618, yields on reduction 3-*amino*-1-*methyl*cyclo*hexane*, b. p. 152—153°/752 mm., D_4^{19} 0·8562, n_D^{19} 1·4558, which is optically inactive, and gives a *benzoyl* derivative, m. p. 95—97°. As a by-product in the formation of the amine, 1-methyl*cyclo*hexan-2-one, $C_7H_{12}O$, is obtained; the latter compound is also formed by the oxidation of an alkaline solution of the nitro-compound with potassium permanganate, or by the action of sulphuric acid on the potassium nitro-compound. It has b. p. 168—169° (corr.), D_4^{17} 0·9179, n_D^{17} 1·4453, and yields two *semicarbazones*, m. p. 179—180° and 167—169°. When oxidised with permanganate, the nitro-compound yields α- and β-methyladipic acids.

Nitro*cyclo*hexane, b. p. 123—124°/40 mm., D_4^{18} 1·0459, n_D^{18} 1·4684, seems identical with the substance obtained by Zelinsky (Abstr., 1908, i, 864). When oxidised, it yields adipic acid. Besides nitro-compounds, nitric acid, when acting on methyl*cyclo*hexane, yields a number of oxidation products, namely, adipic, succinic, oxalic, glutaric, and pyrotartaric acids. The nature of the oxidation processes is discussed.

The nitro-compound from naphtha methyl*cyclo*hexane could not be obtained pure. The impure product has b. p. 109—110°/40 mm., D_4^{20} 1·0254, D_4^0 1·0430, n_D^{20} 1·4553. With tin and hydrochloric acid it gave an *amine*, b. p. 143—145°/755 mm., D_4^0 0·8632, D_4^{17} 0·8493, n_D^{17} 1·4509, the *benzoyl* derivative, $C_7H_{13}\cdot NH\cdot COPh$, of which has m. p. 99—100°. Z. K.

Reduction of Nitro-derivatives by Spongy Copper. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1910, [iv], 7, 952—956).—Bougault has observed (Abstr., 1909, ii, 310; compare Bach, this vol., ii, 31) that sodium hypophosphite added to copper sulphate solution furnishes a precipitate of spongy copper, which, in presence of sodium hypophosphite, decomposes water, liberating hydrogen. This process has been applied to the reduction of nitro-derivatives dissolved in alcohol, and gives good yields, complete in some cases, of the corresponding amines. The presence of halogen atoms or hydroxy-groups in the nitro-derivatives does not impede the reaction, and the halogen or hydroxy-group remains unattacked in the aromatic nucleus. The reaction is likely to be useful in the manu-

facture of aminophenols. Reduction is not effected when hydrogen under pressure is applied to a suspension of spongy copper in a solution of a reducible substance.

The substance to be reduced is dissolved in alcohol and placed in a flask with spongy copper. The flask is provided with a stopper carrying a reflux apparatus, and a bromine tube holding a supply of sodium hypophosphite solution, which is added from time to time as the action slackens. The nitro-derivatives tried include the following: nitroethane, *o*- and *p*-nitrotoluene, *o*-chloronitrobenzene, *p*-bromonitrobenzene, nitronaphthalene, *o*-nitrophenol, and 2 : 3-dinitrophenol.

T. A. H.

Spontaneous Decomposition of Phenylnitromethane. OTTO DIMROTH (*Ber.*, 1910, **43**, 2767—2768).—Crystals of dibenzhydroxamic acid, m. p. 161°, were obtained in quantity from phenylnitromethane preparations which had been kept for a long time. E. F. A.

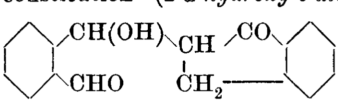
Some New Derivatives of Diphenylmethane. LUIGI MASCARELLI, B. TOSCHI, and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 338—342. Compare Mascarelli, this vol., i, 725).—4 : 4′-*Dichloro*-2 : 2′-*dinitrodiphenylmethane*, obtained by means of the Sandmeyer reaction from the corresponding diamino-derivative, forms slightly yellow, rhombic tablets, m. p. 121—122°. On reduction with tin and hydrochloric acid in alcoholic solution it yields 4 : 4′-*dichloro*-2 : 2′-*diaminodiphenylmethane*, which crystallises in colourless needles, m. p. 130—131°. When diazotised and treated with potassium iodide, it is converted into 4 : 4′-*dichloro*-2 : 2′-*di-iododiphenylmethane*, which forms colourless crystals, m. p. 77—78°.

2 : 2′-*Di-iodo*-4 : 4′-*tetramethyldiaminodiphenylmethane*,

$$NMe_2 \cdot C_6H_3I \cdot CH_2 \cdot C_6H_3I \cdot NMe_2,$$

can be obtained, but only in small amount, by diazotising the corresponding amino-compound and treating it with potassium iodide. It forms colourless scales, m. p. 123°. R. V. S.

Derivatives of *iso*Naphthafluoren (*o*-Phenylene-ββ-naphthylenemethane). JOHANNES THIELE and ALEXIS WANSCHEIDT (*Annalen*, 1910, **376**, 269—279).—A modification of Kipping's method of preparing α-hydrindone (Trans., 1894, **65**, 485) from β-phenylpropionyl chloride (which is best prepared by warming β-phenylpropionic acid with thionyl chloride) is described, whereby the ketone is obtained in 95% yield. It reacts with *o*-phthalaldehyde and 10% sodium hydroxide in aqueous alcohol to form an additive *compound*, $C_{17}H_{14}O_3$, m. p. 185° (decomp.), which receives the annexed constitution (2-ω-*hydroxy*-o-*aldehydobenzyl*-1-*hydrindone*) because it



reduces ammoniacal silver nitrate and is converted into *iso*naphthafluorenone (*o*-phenylene-ββ-naphthylene ketone) (Abstr., 1909, i, 929) by boiling methyl-alcoholic potassium hydroxide. A better method is described for the preparation of *iso*naphthafluorenone. It forms an *oxime*, m. p. 231°, and by reduction with sodium amalgam or with zinc and potassium hydroxide, is converted into iso*naphthafluorenol*,

$\mathrm{OH\cdot CH}<\begin{array}{l}C_6H_4\\ |\\ C_{10}H_6\end{array}$, m. p. 185°. This alcohol forms an *ether*, $O(C_{17}H_{11})_2$ (?), m. p. about 300°, an *acetate*, m. p. 97°, and in glacial acetic acid is converted by hydrogen chloride into the *chloride*, $C_{17}H_{11}Cl$, m. p. 150°, and by hydrogen bromide in glacial acetic acid into the *bromide*, $C_{17}H_{11}Br$, m. p. 162° (decomp.), which is reduced to iso*naphthafluoren*, $C_{17}H_{12}$, m. p. 208°, by zinc and acetic and hydrochloric acids. *Diiso*naphthafluorenyl*, $\begin{array}{l}C_{10}H_6\\ |\\ C_6H_4\end{array}>\mathrm{CH\cdot CH}<\begin{array}{l}C_{10}H_6\\ |\\ C_6H_4\end{array}$, m. p. 260—270° (decomp.), is obtained by heating *iso*naphthafluorenyl bromide and sodium iodide in acetone. *Bisphenylene-bis-ββ-naphthylen-ethylene*, $\begin{array}{l}C_{10}H_6\\ |\\ C_6H_4\end{array}>\mathrm{C{:}C}<\begin{array}{l}C_{10}H_6\\ |\\ C_6H_4\end{array}$, m. p. 232°, obtained by the interaction 5*N*-methyl-alcoholic potassium hydroxide and *iso*naphthafluorenyl bromide in an excess of acetone, crystallises in dark red leaflets; it can also be prepared by heating *iso*naphthafluoren or di*iso*naphthafluorenyl with lead oxide at 300°, and is reduced to the latter by sodium amalgam and boiling amyl alcohol. C. S.

Dinaphthylmethane and Naphthafluorene. JULIUS SCHMIDLIN and MAX HUBER (*Ber.*, 1910, **43**, 2824—2837).—The three dinaphthylmethanes which are theoretically possible are all known, but the constitution of only one has been determined with certainty, namely, di-β-naphthylmethane, m. p. 92°, prepared by reducing di-β-naphthyl ketone (Richter, Abstr., 1881, 281). It is now shown that the hydrocarbon obtained by Grabowski (Abstr., 1875, 455) by condensing naphthalene with methylal in the presence of sulphuric acid is di-α-naphthylmethane, since it can be prepared from di-α-naphthylcarbinol by converting the latter into di-α-naphthylacetic acid, and distilling the acid when carbon dioxide is eliminated. The hydrocarbon described by Claus and Ruppel (Abstr., 1890, 510) must therefore be αβ-dinaphthylmethane.

The constitutions of the isomeric dinaphthaxanthones have also been established. The three isomerides formed from β-naphthol must have the O-bridge in the β-position in both naphthalene rings. The compound with m. p. 149° (Claus and Ruppel, *loc. cit.*) yields αβ-dinaphthylmethane when reduced, and must therefore be *dinaphthylene-αβ-ketone-ββ-oxide*, $\begin{array}{l}C_6H_4\text{——}C\cdot CO\cdot C{:}CH\\ |\qquad\quad\ \, \|\qquad\quad |\\ CH{:}CH\cdot C\text{—}O\text{—}C{:}CH\end{array}>C_6H_4$. Bender's β-dinaphthaxanthone, m. p. 194° (Abstr., 1887, 37), must have the carbonyl group in the α-position with respect to one naphthalene ring (Kostanecki, Abstr., 1892, 1098), and since it is not identical with Claus and Ruppel's xanthone, the carbonyl group must be in the α-position with respect to the second naphthalene ring, and the compound is therefore *dinaphthylene-αα-ketone-ββ-oxide*,

$$\begin{array}{l}C_6H_4\text{——}C\cdot CO\cdot C\text{——}C_6H_4\\ |\qquad\quad\ \, \|\qquad\ \, \|\qquad\quad |\\ CH{:}CH\cdot C\text{—}O\text{—}C\cdot CH{:}CH\end{array}.$$

γ-Dinaphthaxanthone, m. p. 241° (Kostanecki, *loc. cit.*), must be *dinaphthylene-ββ-ketone-ββ-oxide*, $C_6H_4<\begin{array}{l}CH{:}C\cdot CO\cdot C{:}CH\\ \qquad\ \ |\qquad\quad\ |\\ CH{:}C\text{—}O\text{—}C{:}CH\end{array}>C_6H_4$.

Di-a-naphthylacetic acid, $(C_{10}H_7)_2CH\cdot CO_2H$, obtained by converting di-α-naphthylcarbinol (Schmidlin and Massini, Abstr., 1909, i, 561) into the carbinyl chloride, and then condensing this with magnesium and carbon dioxide, has m. p. 223°, and when heated at 250—260° and then at 300° yields di-α-naphthylmethane, m. p. 105° (corr.). Grabowski's hydrocarbon has the same melting point, and in its preparation according to Grabowski's method appreciable amounts of a *compound*, $C_{40}H_{32}O$, are obtained.

β-Iodonaphthalene is prepared readily by a modification of Jacobson's method (Abstr., 1881, 736), and the magnesium β-naphthyl iodide reacts with a dry ethereal solution of ethyl formate, yielding a product which is decomposed by dilute acid, giving di-β-naphthylcarbinol, β-dinaphthafluorene, naphthalene, and another product.

ββ-Dinaphthafluorene, $\begin{matrix}C_{10}H_6\\ | \\ C_{10}H_6\end{matrix}\!\!>CH_2$ is somewhat sparingly soluble in cold ether, but is more soluble than the carbinol in hot light petroleum. It crystallises in large, colourless, nacreous plates, m. p. 190·5° (corr.), and its solutions do not fluoresce. It is isomeric with Bamberger and Chattaway's picylenemethane (Abstr., 1895, i, 293), and when oxidised with an acetic acid solution of chromic anhydride yields *ββ-dinaphthafluorenone*, $\begin{matrix}C_{10}H_6\\ | \\ C_{10}H_6\end{matrix}\!\!>CO$, which crystallises from ether in large, orange-coloured needles, m. p. 163—165° (corr.). The ketone dissolves in concentrated sulphuric acid, yielding deep blue-coloured solutions, which turn brown when kept. The isomeric *αα-dinaphthafluorenone*, prepared by oxidising $\alpha\alpha$-dinaphthafluorene (Schmidlin and Massini, *loc. cit.*), crystallises in minute, deep red-coloured needles, m. p. 255°, and dissolves in concentrated sulphuric acid to red solutions.

Di-β-naphthylcarbinol, $CH(C_{10}H_7)_2\cdot OH$, crystallises from light petroleum (b. p. 110—150°) in nodular masses, m. p. 91° (corr.), containing petroleum of crystallisation. The carbinol also forms a definite *compound* with hexane, $C_{21}H_{16}O,2C_6H_{14}$; this has m. p. 116·5° (corr.), and the hexane is removed when the crystals are heated at 150° under reduced pressure. The carbinol has not been obtained in a crystalline form free from hydrocarbon of crystallisation.

Di-β-naphthylchloromethane, $CH(C_{10}H_7)_2Cl$, obtained by the action of hydrogen chloride on a warm benzene solution of the carbinol, crystallises in colourless prisms, m. p. 167° (corr.). Its solution in concentrated sulphuric acid is colourless, but gradually assumes a violet coloration, due to the formation of the carbinol. It reacts with water or concentrated sulphuric acid less readily than the isomeric $\alpha\alpha$-compound does. *Di-β-naphthylacetic acid*, $CH(C_{10}H_7)_2\cdot CO_2H$, crystallises from glacial acetic acid in felted needles, m. p. 182—183° (corr.), and yields a sparingly soluble *sodium* salt. In the preparation of the acid an appreciable amount of *tetra-β-naphthylethane*,

$$CH(C_{10}H_7)_2\cdot CH(C_{10}H_7)_2,$$

is formed. It crystallises from benzene in small prisms, m. p. 273·5° (corr.).

Tetra-α-naphthylethane (Schmidlin and Massini, *loc. cit.*), when

oxidised with chromic anhydride, yields an *oxide*, $C_{42}H_{28}O$, in the form of orange-red crystals, m. p. 257°.

Attempts to prepare di-α-naphthylketen-quinoline were unsuccessful.

Attempts to prepare tri-β-naphthylcarbinol by the action of β-naphthoyl chloride on magnesium β-naphthyl bromide gave an appreciable amount of an impure hydrocarbon, probably tri-β-naphthylmethane, m. p. 178°. J. J. S.

Some Amide Derivatives of Thiocarbcglycollic Acid. BROR HOLMBERG and B. PSILANDERHIELM (*J. pr. Chem.*, 1910, [ii], 82, 440—450. Compare this vol., i, 361).—In the production of rhodanins from dithiocarbamates and chloroacetamide (Miolati, Abstr., 1893, i, 405), the authors find that the amino-group of the acetic acid derivative is always eliminated by the ring closure, the thiocarbamyl group exhibiting remarkable stability. This conclusion is drawn from experiments on the behaviour of chloroacetamide and of chloroacetanilide on *N*-substituted dithiocarbamates; thus, chloroacetamide reacts easily with aqueous potassium phenyldithiocarbamate (prepared from aqueous potassium hydroxide, aniline, and carbon disulphide, a little *s*-diphenylthiocarbamide, which is formed, being removed by filtration) to form *N*-phenylrhodanin. Chloroacetanilide and aqueous ammonium dithiocarbamate give, according to the conditions of the experiment, either thiocarbamylthioglycollanilide (which is converted into rhodanine by hot dilute sulphuric acid) or a mixture of trithiocarbodiglycollanilide and thiodiglycollanilide; alcoholic chloroacetanilide and aqueous ammonium dithiocarbamate yield only thiodiglycollanilide. Chloroacetamide and aqueous potassium *o*-tolyldithiocarbamate yield *N*-*o*-tolylrhodanine.

Phenylmethylthiocarbamylthioglycollic acid, $CO_2H\cdot CH_2\cdot S\cdot CS\cdot NPhMe$, m. p. 197—198° (decomp.), is obtained by heating aqueous trithiocarbodiglycollic acid and methylaniline, or, much better, by treating aqueous potassium phenylmethyldithiocarbamate with aqueous sodium chloroacetate and acidifying after one day; it forms an *ethyl* ester, m. p. 77°. The *amide*, $NPhMe\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH_2$, m. p. 141—141·5°, obtained from chloroacetamide and aqueous potassium phenylmethyldithiocarbamate, is converted into the free acid by hot dilute sulphuric acid, and into the ethyl ester by alcoholic sulphuric acid. The *anilide*, $NPhMe\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NHPh$, m. p. 139—139·5°, obtained from chloroacetanilide and potassium phenylmethyldithiocarbamate, is unchanged by hot dilute sulphuric acid, and is converted into the ethyl ester by alcoholic sulphuric acid.

Ethyl xanthoacetoanilide, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NHPh$, m. p. 91·5—92°, obtained from chloroacetanilide and potassium xanthate in aqueous-alcoholic solution, and *ethyl trithiocarboglycollanilide*,

$$NHPh\cdot CO\cdot CH_2\cdot S\cdot CS_2Et,$$

m. p. 98°, obtained from chloroacetanilide and potassium ethyl trithiocarbonate, do not yield *N*-phenylrhodanine by elimination of alcohol and ethyl mercaptan respectively. C. S.

Isomerism in Compounds with Two Similar Asymmetric Nitrogen Atoms. EDGAR WEDEKIND and OTTO WEDEKIND (*Ber.*, 1910, 43, 2707—2719).—*Trimethylene*-bis (*phenylmethylethylammonium*

iodide), $CH_2(CH_2 \cdot NMeEtPhI)_2$, has been prepared in two ways: by the action of 2 mols. of methyl iodide on trimethylene-bis-ethylaniline, and by the addition of ethyl sulphate to trimethylene-bis-methylaniline, and interaction of the product with potassium iodide. In both cases the product obtained was a mixture of two isomeric iodides, a small quantity of a monomethiodide being also formed by the first method. The difference between the two iodides persists in their derivatives: those derived from the less fusible iodide are distinguished as *meso-*, those from the more fusible iodide as *para*-compounds. The meso-*iodide* has decomp. 222°, and crystallises in transparent prisms; the para-*iodide* forms opaque, prismatic aggregates (decomp. 177°). The meso-*platinichloride* forms monoclinic plates (decomp. 222°); the isomeride crystallises in monoclinic prisms, also m. p. 222°. The meso-*aurichloride* has decomp. 215°; the para-compound, decomp. 205—206°. The meso-*picrate* has m. p. 129°, forming indefinite crystals; the transparent prisms of the para-*picrate* show m. p. 165°. The meso-d-*camphorsulphonate* forms prismatic needles, m. p. 118—120°; the para-isomeride is very similar, m. p. 116—118°. The meso-d-*bromocamphorsulphonate* is crystalline, m. p. 163°; the isomeride is amorphous.

It has not been possible to transform salts of one series into the other.

Fractional crystallisation of the camphorsulphonates and bromocamphorsulphonates did not resolve either base into optically active forms.

Trimethylene-bis-ethylaniline (compare Fröhlich, Abstr., 1907, i, 346) has b. p. 240—242°/20 mm.

Trimethylene-bis-(phenyldimethylammonium iodide) crystallises in needles (decomp. 216°). E. F. A.

Electrolytic Reduction of Aromatic Sulphonyl Chlorides. FRITZ FICHTER and WALTER TAMM (*Ber.*, 1910, **43**, 3032—3038. Compare this vol., i, 20).—Suspensions of various aromatic sulphonyl chlorides in alcoholic sulphuric acid were reduced at a rotating lead cathode in a divided cell, the temperature being kept down by using a coiled lead tube, through which cold water flowed, as the anode. The most favourable current density varies from 0·04—0·07 ampere per sq. cm.; a further increase in the current density simply leads to the evolution of hydrogen. A copper cathode gives practically the same yield as one of lead, but with cathodes of silver, iron, zinc, nickel, or platinum the yield decreases in the order mentioned. Usually about one and a-half times the theoretical current was passed, the resulting product being a mixture of the disulphide, mercaptan, and sulphinic acid. To isolate these the reaction mixture was made alkaline with ammonia and the mercaptan oxidised by a current of air. After collecting the disulphide, sodium nitrite was added to the filtrate, and, after acidification with dilute sulphuric acid, a precipitate of the diarylsulphonylhydroxylamine derived from the sulphinic acid was obtained. These compounds are generally readily soluble in alkalis or alcohol, but sparingly so in benzene or ether.

α-Naphthalenesulphonyl chloride gave a yield of 81·3% of α-naphthyl disulphide and 13·6% of α-naphthalenesulphinic acid. The *di-α-naphthyl-*

sulphonylhydroxylamine, $(C_{10}H_7\cdot SO_2)_2N\cdot OH$, forms crystals, which have m. p. 120—130° (decomp.). The solutions decompose on warming into tri-α-naphthylsulphonamide. β-Naphthalenesulphonyl chloride gave an 80% yield of the β-naphthyl disulphide and 12·6% yield of β-naphthalenesulphinic acid. *Di-β-naphthylsulphonylhydroxylamine* separated as almost colourless crystals from dilute alcohol; it decomposes at 134°. From benzene-1 : 3-disulphonyl chloride, dithioresorcin was isolated by extracting the weakly acid solution with ether; yield 20—25%. The yield of benzene-1 : 3-disulphinic acid was 50%. Molecular-weight determinations in acetone of the corresponding disulphonylhydroxylamine showed it to be *bis*-m-*phenylenedisulphonylhydroxylamine*, $C_6H_4{<}{\substack{SO_2\cdot N(OH)\cdot SO_2\\ SO_2\cdot N(OH)\cdot SO_2}}{>}C_6H_4$; colourless crystals, decomposing at 212°.

p-Anisolesulphonyl chloride gave a 25·7—37% yield of p-methoxyphenyl disulphide. *Di*-p-*methoxybenzenesulphonylhydroxylamine* forms white needles, m. p. 120° (decomp.). *m*-Nitrobenzenesulphonyl chloride gave a 65—70% yield of *m*-aminophenyl disulphide sulphate.

The reaction mixture resulting from the interaction of sodium dimethylanilinesulphonate and phosphorus pentachloride was shown to contain the sulphonyl chloride by the preparation from it of p-*dimethylanilinesulphonanilide*, $NMe_2\cdot C_6H_4\cdot SO_2\cdot NHPh$; colourless crystals from alcohol, m. p. 176°. The crude reaction mixture containing the sulphonyl chloride gave *dithiodimethylaniline*, $S_2(C_6H_4\cdot NMe_2)_2$, on electrolytic reduction; m. p. 118°. The yield is very small because of the instability of the sulphonyl chloride. T. S. P.

Theory of Organic Reactions. Molecular Compounds as Preliminary Products in Cases of Condensation. I. JULIUS SCHMIDLIN and RUDOLF LANG (*Ber.*, 1910, **43**, 2806—2820. Compare Uroczynski and Guye, this vol., ii, 699).—The authors accept Fittig's view that chemical reactions are preceded by the formation of more or less unstable additive compounds (compare Michael, Abstr., 1888, 1055; 1900, i, 321; 1904, ii, 64), and attention is drawn to the fact that in the case of triphenylmethyl derivatives and nitrosodimethylaniline chemical reactivity is accompanied by capacity for formation of additive compounds.

The examples investigated have been those of condensations which take place readily in the presence of a condensing reagent without the application of heat. In such cases the question is not complicated to any appreciable extent by the formation of additive compounds between the reacting substances and the condensing agent. The following pairs of substances have been examined: phenol and acetone, resorcinol and acetone, quinol and acetone, catechol and acetone, pyrogallol and acetone, and phenol and *cyclo*hexanone. In those cases in which condensation takes place with great readiness, it is found that additive compounds are formed, and that the relative amounts of the components in the additive compound are the same as the relative proportions in which they react to form the condensation product. Catechol and acetone, and also quinol and acetone, condense but slowly in the presence of concentrated hydrochloric acid and the additive compounds,

and condensation products bear no simple relationship to one another. In the latter case, the question is complicated by the formation of a definite *compound* of quinol with hydrogen chloride,

$$3C_6H_4(OH)_2,HCl.$$

Similarly, the additive compounds and condensation products of pyrogallol and acetone, and of phenol and *cyclo*hexanone, do not correspond.

In some cases the additive compounds have been actually isolated, and in all cases have been detected by melting-point curves.

Phenol and acetone yield the *compound*, $2Ph{\cdot}OH,COMe_2$, in the form of long needles, m. p. 15°, and the condensation product, di-*β*-*p*-hydroxyphenylpropane, $CMe_2(C_6H_4{\cdot}OH)_2$ (compare Dianin, Abstr., 1893, i, 214; Zincke and Grüters, *ibid*, 1906, i, 172), which is formed most readily when cold concentrated sulphuric acid is used as condensing agent. When crystallised from benzene, it retains benzene of crystallisation, $3C_{15}H_{16}O_2,C_6H_6$, which it loses when heated at 80° under reduced pressure.

Resorcinol and acetone yield the *compound*, $C_6H_4(OH)_2,2COMe_2$, m. p. 28°, which is comparatively stable. In determining melting points of mixtures of the two compounds, it is essential to avoid the entrance of traces of moisture, as such traces cause the mixtures to set to solid vitreous masses. The condensation product has not the composition stated by Causse (Abstr., 1892, 1312), but is to be represented as $C_{12}H_{14}O_2$. $C_6H_4(OH)_2+2CO(CH_3)_2=C_{12}H_{14}O_2+2H_2O$, and has m. p. 230—240°.

Catechol and acetone yield a somewhat unstable *compound*,

$$C_6H_4(OH)_2,COMe_2,$$

m. p. −30°. The *condensation product* has the formula $C_{15}H_{14}O_4$, is formed in only small quantities, and decomposes at 270°. Quinol and acetone yield the *compound*, $C_6H_4(OH),COMe_2$, when sealed tubes are used (compare Habermann, Abstr., 1885, 53). Pyrogallol and acetone yield the *compound*, $C_6H_3(OH)_3,3COMe_2$, m. p. −24°. The *condensation product* contains C = 68·4 and H = 6·3%.

The *compound* of phenol and *cyclo*hexanone, $PhOH,C_6H_8O$, has m. p. −23°, and the condensation product, 1 : 1-*di*-p-*hydroxyphenyl*cyclo*hexane*, $C_6H_{10}(C_6H_4{\cdot}OH)_2$, obtained by using concentrated sulphuric acid, crystallises in colourless, rhombic plates containing alcohol, m. p. 186° (corr.).

a-Naphthol and *cyclo*hexanone react with concentrated sulphuric acid, yielding a *product*, $C_{26}H_{22}O$, m. p. 232°. This appears to be the anhydride of di-*a*-hydroxynaphthyl*cyclo*hexane, $C_6H_{10}{<}{\substack{C_{10}H_6\\C_{10}H_6}}{>}O$, and is insoluble in alkalis.

J. J. S.

An Easy Transformation of Asaryl Aldehyde into a Triphenylmethane Derivative. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1910, **43**, 2676—2684).—A good yield of *nonamethoxytriphenylmethane*, $CH[C_6H_2(OMe)_3]_3$, is obtained when asaryl aldehyde is heated with 25% hydrochloric acid for three hours on a water-bath. It may be freed from a brown, amorphous by-product by treatment with very dilute alkali hydroxide, and separates from alcohol in

colourless crystals, m. p. 184·5°. Its solution in sulphuric acid has a brilliant blue colour, and the crystals tend to turn yellow when kept in a calcium chloride desiccator. Concentrated nitric acid reacts with a glacial acetic acid solution of the nonamethoxy-derivative, yielding 4-nitro-1 : 2 : 5-trimethoxybenzene (Abstr., 1907, i, 45). Bromine reacts with a cold benzene solution of the nonamethoxytriphenylmethane according to the equation :

$$CH[C_6H_2(OMe)_3]_3 + 2Br_2 = C_6H_2Br(OMe)_3 + C_{19}H_{23}O_6Br_3.$$

The 4-*bromo*-1 : 2 : 5-*trimethoxybenzene* crystallises from alcohol in colourless, monoclinic prisms [$a:b = 0·97506:1$; $\beta = 50°56'$], m. p. 54·5°. The same compound can be prepared more readily by the action of bromine on asaronic acid, or by the bromination of hydroxyquinol trimethyl ether. In the latter case, when an excess of bromine is used, dark blue, glistening crystals, $C_9H_{11}O_3Br_2$, are formed, but these are extremely unstable, and with water yield the bromotrimethoxybenzene. The second product, obtained by the action of bromine on the nonamethoxy-derivative, crystallises from benzene in slender prisms with a dark purple-blue colour, and is represented as a *bromine* additive compound of *hexamethoxydiphenylmethane*, namely,

$$BrMeO:C<\begin{matrix}C(OMe):CH\\CH:C(OMe)\end{matrix}>C:CH\cdot CBr<\begin{matrix}C(OMe):CH\\CH:C(OMe)\end{matrix}>C:OMeBr.$$

This formula is supported by the fact that the compound reacts with water, yielding asarylaldehyde and bromotrimethoxybenzene,

$$C_{19}H_{23}O_6Br_3 + H_2O = CHO\cdot C_6H_2(OMe)_3 + C_6H_2Br(OMe)_3.$$

Dibromotrimethoxybenzene, $C_6HBr_2(OMe)_3$, prepared by the action of bromine on the monobromo-derivative, crystallises from benzene in long, colourless needles, m. p. 61°. 2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethoxydiphenyl*, $C_{12}H_4(OMe)_6$, can be obtained from the bromotrimethoxybenzene and copper at 270°. It crystallises from alcohol, has m. p. 180°, and yields a greenish-blue, unstable, additive compound with benzene.

2 : 4 : 5 : 2′ : 4′ : 5′-*Hexamethoxydiphenylacetonitrile*,

$$CN\cdot CH[C_6H_2(OMe)_3]_2,$$

is formed by the action of silver cyanide on the bromine additive compound of hexamethoxydiphenylmethane : $C_{19}H_{23}O_6Br_3 + 3AgCN = CN\cdot CH[C_6H_2(OMe)_3]_2 + 3AgBr + C_2N_2$, and crystallises from alcohol in slender needles, m. p. 155°.

Hydrogen chloride yields a deep blue additive compound with the nonamethoxytriphenylmethane, and when this is decomposed with water a colourless compound, m. p. 115—116°, is formed. J. J. S.

cycloButylcarbinol (ω-Hydroxymethylcyclobutane) and its Isomerisation Under the Influence of Acids into Pentane Derivatives. NICOLAUS J. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 837—855. Compare Abstr., 1903, i, 403; Perkin, Trans., 1901, **79**, 329).—The most convenient method of obtaining *cyclo*butylcarbinol, $C_4H_7\cdot CH_2\cdot OH$, is by the reduction of ethyl *cyclo*butanecarboxylate with metallic sodium in alcoholic solution. When pure, it has b. p. 140—142·5°/750 mm., D_{10}^{10} 0·9199, D_{20}^{20} 0·9129, n_D^{20} 1·4449. When oxidised with chromic anhydride and sulphuric acid, it forms an *aldehyde*, of which the *sodium bisulphite* compound and a *semi*-

carbazone, m. p. 115—120°, were prepared in an impure state, and cyclo*butylcarbinyl* cyclo*butanecarboxylate*,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}CH\cdot CO_2\cdot CH_2\cdot CH{<}{}^{CH_2}_{CH_2}{>}CH_2,$$

b. p. 218—220°, D_{19}^{19} 0·9795, n_D^{19} 1·4546, n_D^{21} 1·4533.

When heated with hydrogen bromide in a sealed tube at 100°, *cyclo*butylcarbinol is converted into *bromo*cyclo*pentane*,

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}{>}CHBr,$$

b. p. 137—139°, D_{19}^{19} 1·385, n_D^{19} 1·4875, which by means of zinc palladium and hydrobromic acid is reduced to *cyclo*pentane, b. p. 49—50°/750 mm., $D_{18·5}^{18·5}$ 0·7525, $D_{20·5}^{20·5}$ 0·7513, $n_D^{18·5}$ 1·4087, $n_D^{20·5}$ 1·4072.

*Iodo*cyclo*pentane*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}{>}CHI$, prepared similarly, is a colourless liquid, which turns green or brown when kept, has b. p. 162—164°/750 mm. (decomp.), D_4^0 1·7154, $D_4^{21·5}$ 1·6825, n_D^{22} 1·5374, and with silver nitrate yields a secondary and a primary nitro-compound, which, without being isolated, were converted into the ψ-nitrole, $NO\cdot C_5H_8\cdot NO_2$, m, p. 96°.

With oxalic acid, *cyclo*butylcarbinol yields a hydrocarbon, b. p. 43·5—44°/755 mm., seemingly identical in physical properties with that obtained from ω-aminomethyl*cyclo*butane, and probably consisting of a mixture of *cyclo*pentene, $\begin{matrix}CH_2-CH\\ |\\ CH_2\cdot CH_2\end{matrix}{\gg}CH$, and a dicyclo*pentene*, $\begin{matrix}CH_2\cdot CH\\ |\quad\ \ |\\ CH_2\cdot CH\end{matrix}{>}CH_2$, or of the latter only.

The unsaturated hydrocarbon gives a *dibromide*, b. p. 192—195°, and with sulphuric acid an *alcohol*, b. p. 137—138°/753 mm., which with chromic anhydride and sulphuric acid yields *cyclo*pentanone, b. p. 130—131·5°, from which the oxime, m. p. 57°, and dibenzyl derivative, m. p. 189°, were prepared. The constitution of the unsaturated hydrocarbon and the isomerisation of *cyclo*butanes into *cyclo*pentanes is discussed. Z. K.

The Fluorene Series. A Correction. JULIUS SCHMIDT (*Ber.*, 1910, **43**, 2778—2779).—The substance described as fluorene ether by Schmidt and Stützel (this vol., i, 29) is, as Kliegl (this vol., i, 733) has in the meantime shown, a mixture of red dibiphenylene-ethylene and colourless diphenylenephenanthrone. E. F. A.

9-Formylfluorene or Diphenyleneacetaldehyde [Fluorene-9-aldehyde]. II. WILHELM WISLICENUS and KARL RUSS (*Ber.*, 1910, **43**, 2719—2734. Compare Abstr., 1909, i, 241).—In the pure state only the crystalline β-form and the polymeride of double molecular weight exist; the oily α-form is in reality the β-form hindered from crystallisation by impurities. Formylfluorene tends to polymerise when distilled; the vapour is unimolecular, but it polymerises during cooling. The enolic form is unstable, and no ferric chloride coloration is

produced. The enolic potassium compound gives no coloration, but a precipitate of ferric hydroxide.

The *sodium bisulphite* compound crystallises in colourless, flat needles, m. p. 151—152° (decomp.). The *O*-acetate crystallises in platelets, m. p. 132—133°, and forms a *dibromide*,

$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CBr\cdot CHBr\cdot OAc,$$

separating in colourless plates, m. p. 146—147° (decomp.). By the action of dry ammonia, a colourless compound, m. p. 148—149°, is formed, either *iminomethylfluorene*, $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CH\cdot CH{:}NH$, or *aminomethylenefluorene*, $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>C{:}CH\cdot NH_2$. When heated above the melting point, a yellow compound is formed, which crystallises from nitrobenzene in small, golden-yellow prisms, m. p. 316—317°.

This dissolves in alcoholic potassium hydroxide or sodium ethoxide with a bluish-red coloration, which slowly disappears on standing; this colour change is attributed to conversion into the desmotropic form.

Formylfluorenemonoethylanilide, $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>C{:}CH\cdot NEtPh$, prepared by interaction of the components, crystallises in slender, canary-yellow prisms, m. p. 95—96°. The corresponding *piperidine* derivative, prepared in alcoholic solution, crystallises in yellow plates.

Formylfluorene-α-oxime, $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CH\cdot CH{:}N(OH)$, probably the *anti*-form, crystallises in colourless needles, m. p. 132—133°, colouring at 166°. The *β-oxime*, probably the *syn*-form, crystallises in similar needles, m. p. 166—167°.

9-*Cyanofluorene* [*fluorene*-9-*carboxylonitrile*], $\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CH\cdot CN$, produced by the action of thionyl chloride on the oxime, forms long, lustrous, colourless needles, m. p. 151—152°. It dissolves in warm sodium hydroxide with a yellow colour and bluish-green fluorescence.

Formylfluorenebenzoylhydrazide separates in lustrous, light yellow needles, m. p. 233—234°. On evaporation of solutions of the phenylhydrazone, an oxidation product, m. p. 155—156°, is formed, probably an *azo*-compound. This reacts with bromine, forming a p-*bromobenzeneazomethylenefluorene dibromide*, $C_{20}H_{13}N_2Br_3$, crystallising in dark red needles, m. p. 210—211°. It is more easily obtained from *formylfluorene*-p-*bromophenylhydrazone*, which crystallises in lustrous, yellow plates, m. p. 158—159° (decomp.), and yields p-*bromobenzeneazomethylenefluorene*, $C_{13}H_8{:}CH\cdot N{:}N\cdot C_6H_4Br$, on oxidation, crystallising in lustrous, deep red needles with a blue reflex, m. p. 187—188°, and dissolving in concentrated sulphuric acid with an intense violet coloration.

Formylfluorenehydrazone forms colourless, lustrous, silky needles, m. p. 158—160°; it readily undergoes oxidation to *azomethylene fluorene*, $C_{13}H_8{:}CH\cdot N{:}N\cdot CH\cdot C_{13}H_8$, crystallising in very dark red, lustrous prisms, with a blue reflex, m. p. 290° (about).

Formylfluorenecyanohydrin forms colourless, slender, silky needles,

m. p. 142—143°. When heated with concentrated hydrochloric acid in sealed tubes at 125°, *fluorene-9-glycollic acid*, $C_{13}H_9\cdot CH(OH)\cdot CO_2H$, is formed in colourless plates, m. p. 194—195°. When boiled with potassium ethoxide, *cyanomethylenefluorene*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C:CH\cdot CN$, is obtained as a yellow, crystalline substance, m. p. 109—110°. It is remarkably stable towards hydrolysing agents.

By the action of bromine on formylfluorene an oil is produced. When dissolved in alcohol, the *acetal*, $C_{18}H_{19}O_2Br$, crystallises in colourless needles, m. p. 119—120°.

Di-biphenylenesuccinaldehyde, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C(CHO)\cdot C(CHO)<\!\!\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$, is obtained on oxidising formylfluorene with ferric chloride in acetic acid solution; it crystallises in colourless, lustrous prisms, m. p 215—216°. Potassium ethoxide converts it into potassium formate and dibiphenylene-ethane. E. F. A.

Formation of an Ethylene Oxide from the Quaternary Base of Phenylmethylhydroxyethylamine. PAUL RABE and JULIUS HALLENSLEBEN (*Ber.*, 1910, **43**, 2622—2623. Compare this vol., i, 317).—It is shown that α-phenylpropylene αβ-oxide is formed when the aqueous solution of Emde and Runne's (this vol., i, 479) base from the methiodide of α-amino-α-phenyl*iso*propyl alcohol is heated.

The *oxide*, $\begin{matrix} CHPh \\ | \\ CHMe \end{matrix}\!\!>O$ (yield 40%), is a colourless liquid, b. p. 200°/752 mm., is heavier than water, and has a characteristic odour. J. J. S.

Unsaturated Hydroaromatic Acids with One Semicyclic Double Linking, and Their Derivatives. KARL AUWERS and G. PETERS (*Ber.*, 1910, **43**, 3094—3110. Compare this vol., i, 826, 827). —When 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-one is condensed with ethyl bromoacetate in presence of zinc and benzene, the product obtained is *ethyl* 1 : 3-*dimethyl*-Δ^3-cyclo*hexene*-5-*ol*-5-*acetate*,

$$CH_2<\!\!\begin{matrix} CMe{=}CH \\ CHMe{-}CH_2 \end{matrix}\!\!>C(OH)\cdot CH_2\cdot CO_2R,$$

b. p. 110°/2·5 mm. or 123°/4·5 mm. (decomp.), $D_4^{16\cdot8}$ 1·0126, $n_\alpha^{17\cdot6}$ 1·46857, $n_D^{17\cdot6}$ 1·47133, $n_\gamma^{17\cdot6}$ 1·48411 (whence $\Sigma_\alpha = +0\cdot27$, $\Sigma_D + 0\cdot20$, and $\Sigma_\gamma - \Sigma_\alpha = 7\%$), is a colourless, viscid oil, which when heated with dehydrating agents furnishes *ethyl* 1 : 3-*dimethyl*-Δ^3-cyclo*hexenylidene*-5-*acetate*, $CH_2<\!\!\begin{matrix} CMe{=}CH \\ CHMe{-}CH_2 \end{matrix}\!\!>C:CH\cdot CO_2Et$, b. p. 111—113°/5·5 mm. or 145—147°/15 mm., D_4^{20} 0·971—0·979, n_α^{20} 1·510—1·513, n_D^{20} 1·516—1·519, $\Sigma_\alpha + 1\cdot79$ to 2·15, $\Sigma_D + 1\cdot87$ to 2·25, and $\Sigma_\gamma - \Sigma_\alpha$ 116 to 123%, which is identical with the substance wrongly assumed by Wallach and Bötticher to be ethyl $\Delta^{1\cdot5}$-dihydro-3 : 5-xylyl-1-acetate, $CH_2<\!\!\begin{matrix} CMe{=}CH \\ CHMe{-}CH \end{matrix}\!\!\gg C\cdot CH_2\cdot CO_2Et$ (Abstr., 1902, i, 798). On hydrolysis with sodium ethoxide, it yields the free acid,

m. p. 153—154°, and this when heated in closed tubes furnishes the corresponding hydrocarbon, 1 : 3-dimethyl-5-methylene-Δ^3-*cyclo*hexene (this vol., i, 826, and Wallach and Bötticher, *loc. cit.*). The acid is reduced with sodium amalgam in presence of carbon dioxide to 1 : 3-*dimethyl*-Δ^4-cyclo*hexene*-5-*acetic acid*, b. p. 154—155°/16·5 mm., $D_4^{20\cdot1}$ 0·9947, n_α 1·47428, n_D 1·47731, n_γ 1·49068 (whence $\Sigma_\alpha + 0\cdot33$, $\Sigma_D + 0\cdot27$, and $\Sigma_\gamma - \Sigma_\alpha = 8\%$), a colourless oil, which is oxidised by permanganate to an *acid*, $C_9H_{15}O_3$, and on treatment with bromine followed by sodium hydroxide solution yields *s*-xylylacetic acid.

Ethyl 1 : 3-dimethyl-Δ^3-*cyclo*hexenylidene-5-acetate when treated with magnesium methyl iodide yields 1 : 3-*dimethyl*-Δ^3-cyclo*hexene*-5 *trimethylcarbinol*, $CH_2<\begin{matrix}CMe{=\!=}CH\\CHMe\text{-}CH_2\end{matrix}>C{:}CH\cdot CMe_2\cdot OH$, b. p. 125—126°/18 mm., D_4^{20} 0·922—0·934, n_α^{20} 1·503—1·506, n_D^{20}, 1·508—1·510 (whence $\Sigma_\alpha = +0\cdot95$ to $+1\cdot23$, $\Sigma_D = +1\cdot00$ to 1·28, and $\Sigma_\gamma - \Sigma_\alpha = 48\%$), which, since it decomposes on heating, could not with certainty be prepared free from the *hydrocarbon*,

$$CH_2<\begin{matrix}CMe{=\!=}CH\\CHMe\text{-}CH_2\end{matrix}>C{:}CH\cdot CMe{:}CH_2,$$

resulting from this decomposition. This hydrocarbon has b. p. 103—106°/17 mm., D_4^{20} 0·862—0·867, n_α^{20} 1·495—1·518, n_D^{20} 1·503—1·533, Σ_α +0·72 to 1·86, Σ_D +0·75 to 2·02, and $\Sigma_\gamma - \Sigma_\alpha$ +25 to 93%. T. A. H.

Bismuth Benzoates. GODFRIN (*J. Pharm. Chim.*, 1910, [vii], **2**, 385—396. Compare Rebière, Abstr., 1896, ii, 396).—Bismuth benzoate and a series of basic bismuth benzoates are described, full details of their method of preparation being given.

Bismuth benzoate, $Bi(OBz)_3$, prepared by double decomposition between bismuth nitrate and sodium benzoate, both salts being dissolved in a mixture of water and glycerol, and a solution of benzoic acid in water being used for washing and re-crystallising the salt, forms bulky, brilliant, colourless, orthorhombic prisms, is stable up to 140°, and is decomposed by water, alcohol, or ether, forming basic salts. Treated in the cold with twenty times its weight of alcohol it furnishes a salt, $Bi_4O_3(OBz)_6$. This is a dead white powder, seen under the microscope to consist of minute, colourless, cubic crystals. It decomposes at about 160°. When treated with twenty times its weight of cold ether or a like quantity of alcohol at 95°, the neutral salt yields a new basic *salt*, $Bi_2O_3(BiO\cdot OBz)_{12}$, a white, partly crystalline powder. All the foregoing when treated with alcohol at 95° furnish the *salt*, $Bi_2O_3(BiO\cdot OBz)_6$, which consists of colourless, microscopic, monoclinic prisms. *Bismuthyl benzoate*, $BiO\cdot OBz$, crystallises in minute, monoclinic prisms. It is stable in air up to 140°, but when treated with alcohol at 95° it decomposes, like the other salts described, furnishing the salt $Bi_2O_3(BiO,OBz)_6$. T. A. H.

Alkylation of Aromatic Amino-acids. IV. Nitroamino- and Iodoamino-acids. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1910, **44**, 5, 441—452. Compare this vol. i, 381, 666). —The investigation of the behaviour of aromatic amino-acids on

ethylation is continued by a study of further acids. 4-Nitro-2-aminobenzoic acid gives a mixture of 40% of the primary amino-ester and 40% of the *N*-alkyl acid. 2-Nitro-4-aminobenzoic acid gives only the ester (43·4%). Both 4-iodo-*o*-aminobenzoic acid and 5-iodo-*o*-aminobenzoic acid give only *N*-alkyl acids (71—76%). 4 : 5-Di-iodo-*o*-aminobenzoic acid alkylates with difficulty, and gives only the ester (28%).

These results show that the tendency of amino-acids to react in an abnormal manner and give esters is not dependent on stereochemical interference.

An improved method for the preparation of 4-nitro-2-aminobenzoic acid is given ; the ethyl ester melts at 100°.

4-*Iodo*-2-*nitrobenzoic acid* forms prisms, m. p. 192°. 4-*Iodo*-2-*aminobenzoic acid* crystallises in flat prisms, decomposing at 208° ; 4-*iodo*-2-*ethylaminobenzoic acid* forms clusters of plates, m. p. 188°. 4-*Iodo*-2-*methylaminobenzoic acid* crystallises in needles, m. p. 197°.

4 : 5-*Di-iodo*-2-*aminobenzoic acid* begins to give off iodine at 200° ; its *ethyl* ester forms slender needles, m. p. 137°. N. C.

Complete Methylation of Some Amino-acids. R. ENGELAND (*Ber.*, 1910, **43**, 2662—2664. Compare Abstr., 1909, i, 856).—When a mixture of phenylalanine (α-amino-β-phenylpropionic acid), methyl-alcoholic potassium hydroxide, and methyl iodide is boiled gently for several hours, the chief product is *phenyl*-N-*trimethylalanine methyl* ester, the *platinichloride* of which, $2C_{13}H_{20}O_2NPtCl_6$, has m. p. 177—178°. The *aurichloride* of *phenyltrimethylalanine*,

$$C_{12}H_{18}O_2N,HAuCl_4,$$

forms golden-yellow needles, m. p. 94—95°.

When α-aminoglutaric acid is treated in a similar manner two products are obtained, the one forms a sparingly soluble *aurichloride*, $C_9H_{17}O_4N,HAuCl_4$, probably derived from the dimethyl ester of dimethylglutamic acid, and the other an *aurichloride*,

$$C_7H_{13}O_4N,HAuCl_4,$$

in the form of readily soluble, hygroscopic crystals, probably derived from dimethylglutamic acid. J. J. S.

Synthesis of Compounds of the Normal Phenylpropane, Phenylbutane, and Phenylpentane Series. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 2837—2852).—The synthesis of compounds containing the group $C_6H_5\cdot[CH_2]_x\cdot$ is important, since it is very probable that many resins contain such fatty-aromatic chains. Methods based on the interaction of sodium and aryl halides, or of aluminium chloride and aromatic hydrocarbons, on substances of the type

$$Cl\cdot[CH_2]_x\cdot Cl$$

or $Cl\cdot[CH_2]_x\cdot OPh$ have proved unsatisfactory. γ-Bromopropylphthalimide and ε-chloroamylphthalimide are very resistent to the attack of sodium, but, contrary to expectation, react with aluminium chloride. The former yields only an additive compound, which is easily decomposed into its generators, but its formation suggests that the usual Friedel-Crafts' reaction might take place with a substance in which the acylated amino-group is removed further from the

halogen atom. This expectation is fulfilled, benzoyl-ε-chloroamylamine and benzoyl-ζ-chlorohexylamine reacting with aluminium chloride and benzene in the usual way. The product of the first reaction is *benzoyl-ε-phenylamylamine*, $C_6H_5\cdot[CH_2]_5\cdot NHBz$, b. p. 273—275°/15 mm., in 90% yield, which is hydrolysed by hydrochloric acid under pressure to *ε-phenylamylamine*, b. p. 131°/15 mm., a colourless liquid which has a faint basic odour, only slowly absorbs water and carbon dioxide from the air, and forms a *platinichloride*,

$$2C_{11}H_{17}N,H_2PtCl_6,$$

decomp. 220°, *picrate*, m. p. 152—153°, *benzoyl* derivative, m. p. 60° (the benzoyl derivative, as obtained in the preparation above, has not been made to crystallise), and a *methiodide*,

$$C_6H_5\cdot[CH_2]_5\cdot NMe_2,MeI,$$

m. p. 181°, the *platinichloride* of which has m. p. 219°. The normal constitution of the ε-phenylamylamine, prepared from benzoyl-ε-chloroamylamine by the Friedel-Crafts' method, is proved by the synthesis of the base by the following series of reactions, which represent the fulfilment of the object of the author's work. *γ-Iodopropylbenzene*, $C_6H_5\cdot[CH_2]_3I$, b. p. 137—140°/20 mm., obtained by the prolonged boiling of γ-chloropropylbenzene and sodium iodide in alcohol, is warmed with an aqueous alcoholic solution of potassium cyanide (2 mols.), whereby *γ-phenylbutyronitrile*, b. p. 142—145°/16 mm., is obtained; the nitrile, by reduction with sodium and alcohol (distilled over sodium and kept for many days, or, better, weeks over calcium), yields *δ-phenylbutylamine*, $C_6H_5\cdot[CH_2]_4\cdot NH_2$, b. p. 123—124°/17 mm. (*platinichloride*, decomp. 205°; *picrate*, m. p. 125°; the N-*dimethyl methiodide*, $C_6H_5\cdot[CH_2]_4\cdot NMe_2,MeI$, m. p. 191—192°), the *benzoyl* derivative of which, m. p. 83·5°, is converted by distillation with phosphorus pentachloride into *δ-chlorobutylbenzene*,

$$C_6H_5\cdot[CH_2]_4\cdot Cl,$$

b. p. 122—123°/17 mm., in 75% yield. This substance, by reactions similar to the preceding, is converted successively into *δ-iodobutylbenzene*, b. p. 148—151°/15 mm., *δ-phenylvaleronitrile*, b. p. 157—161°/17 mm., and ε-phenylamylamine, which is identical with the base prepared above.

By distillation with phosphorus pentachloride, benzoyl-ε-phenylamylamine yields *ε-chloroamylbenzene*, $C_6H_5\cdot[CH_2]_5Cl$, b. p. 134°/18 mm., which has a very pleasant odour, reacts with alcoholic sodium phenoxide to form *phenyl ε-phenylamyl ether*, b. p. 198°/14 mm., and with alcoholic sodium iodide to form *ε-iodoamylbenzene*, b. p. 158—165°/20 mm., in which the presence of the normal amyl chain is proved by the reaction of the iodide with alcoholic trimethylamine, whereby ε-phenylamyltrimethylammonium iodide, m. p. 181°, is obtained, identical with the salt produced by the exhaustive methylation of ε-phenylamylamine.

γ-Chloropropylbenzene is obtained readily from tetrahydroquinoline. The benzoylated base is ruptured by phosphorus pentachloride, and the resulting *o*-γ-chloropropylbenzanilide is hydrolysed to γ-chloropropylaniline, from which the amino-group is eliminated by diazotisation and subsequent treatment with alkaline stannous chloride. γ-Bromopropylbenzene, which is obtained quantitatively from dihydro-

cinnamyl alcohol and fuming hydrobromic acid at 105°, can only be prepared indirectly from γ-chloropropylbenzene; the latter is boiled for many hours with a large excess of alcoholic sodium phenoxide, and the resulting *phenyl γ-phenylpropyl ether*, $CH_2Ph\cdot[CH_2]_2\cdot OPh$, b. p. 182—183°/17 mm., is heated with fuming hydrobromic acid.

C. S.

The Liberation of Carbon Monoxide from the Tertiary Acids Arising from the Condensation of Phenylpyruvic Acid with Aromatic Hydrocarbons. AUGUSTIN BISTRZYCKI and LOUIS MAURON (*Ber.*, 1910, **43**, 2883—2889. Compare Abstr., 1907, i, 1039; Bistrzycki and von Weber, this vol., i, 742).—The investigation of the liberation of carbon monoxide from tertiary acids on treatment with concentrated sulphuric acid has now been extended to some benzyldiarylacetic acids, which have now been prepared from phenylpyruvic acid and aromatic hydrocarbons, using cooled, concentrated sulphuric acid as the condensing agent, in the manner previously described (Bistrzycki and Reintke, Abstr., 1905, i, 285). The acids of this type evolve only two-thirds to three-quarters of the theoretical amount of carbon monoxide, the incompleteness of the reaction being due probably to partial sulphonation. The products obtained are completely soluble in water. Triarylethylenes, analogous to the diarylethylenes of Bistrzycki and Reintke (*loc. cit.*), were not obtained. None of the acids loses carbon dioxide on heating.

*β-Phenyl-αα-di-*p*-tolylpropionic acid*, $CH_2Ph\cdot C(C_6H_4Me)_2\cdot CO_2H$, from toluene and phenylpyruvic acid, crystallises in colourless, lustrous needles or prisms, m. p. 176°. That the phenylpyruvic acid has not reacted in the desmotropic form (compare Ruhemann and Stapleton, Trans., 1900, **77**, 241) follows from the fact that the analogous anisole derivative yields di-*p*-anisyl ketone on oxidation (Lamoni, *Diss.* Freiburg, Switzerland, 1910, 33). The *silver* salt, $C_{23}H_{21}O_2Ag$, was obtained as a white precipitate. The *methyl* ester, $C_{24}H_{24}O_2$, forms hexagonal prisms, m. p. 117°.

*α-Phenyl-ββ-di-*p*-ethylphenylpropionic acid*,

$$CH_2Ph\cdot C(C_6H_4Et)_2\cdot CO_2H$$

(from ethylbenzene), crystallises in rosettes of stout needles or in flat prisms, m. p. 183—184°. The *ethyl* ester, $C_{27}H_{30}O_2$, forms microscopic prisms, m. p. 61°.

*α-Phenyl-ββ-di-*o*-xylylpropionic acid*, $CH_2Ph\cdot C(C_6H_3Me_2)\cdot CO_2H$ (from *o*-xylene), crystallises in four-sided prisms or in needles, m. p. 160°. The *methyl* ester, $C_{26}H_{28}O_2$, forms microscopic prisms, m. p. 96—97°.

Phenylpyruvic acid does not react with *m*-xylene under the conditions stated, or with mesitylene and naphthalene. Only in one instance was it possible to obtain with benzene an acid of the m. p. of the expected αββ-triphenylpropionic acid, whilst the products from cumene and cymene were difficult to purify.

R. V. S.

Comparison of Certain Acids Containing a Conjugated System of Double Linkings. ANNIE LOUISE MACLEOD (*Amer. Chem. J.*, 1910, **44**, 331—352).—Reimer (Abstr., 1907, i, 852) has

shown that when methyl cinnamylidenemalonate is treated with a Grignard reagent, $a\delta$-addition takes place, but on decomposing the product rearrangement occurs, and the hydrogen atom by which the magnesium has been replaced is found to occupy the α-position to the carboxyl group. Reimer and Reynolds (Abstr., 1908, i, 988) have shown that methyl α-phenylcinnamylideneacetate reacts less readily with organic magnesium compounds, and that the resulting products consist chiefly of ketones formed by the replacement of the methoxy-group and subsequent addition of a second molecule of the reagent in the $a\delta$-position. A study has now been made of α-methylcinnamylideneacetic and α-cyanocinnamylideneacetic acids.

α-Methylcinnamylideneacetic acid is pale yellow when first obtained, but becomes white on exposure to light. It has been found that when the yellow form is treated with a very small quantity of sodium amalgam, the yellow colour disappears, and the colourless acid remains. The substance to which the yellow colour is due is therefore present in only small amount, and may possibly be an isomeric form of the acid. When the acid is exposed to direct sunlight for about four days, it is converted into 2 : 4-*diphenyl*cyclo*butane*-1 : 3-*di-α-methylacrylic acid*, $CO_2H \cdot CMe{:}CH \cdot CH{<}{\substack{CHPh \\ CHPh}}{>}CH \cdot CH{:}CMe \cdot CO_2H$, m. p. 253—254°, which forms small, transparent prisms, and, on oxidation with potassium permanganate, yields α-truxillic, benzoic, and oxalic acids ; its *methyl* ester, m. p. 126·5—127°, crystallises in slender needles. The acid unites with bromine with formation of a product which appears to be a mixture of a di- and a tetra-bromide ; the methyl ester gives a *tetrabromide*, m. p. 200—201°.

When methyl α-methylcinnamylideneacetate is treated with bromine in presence of a little iodine, a *tetrabromide*, m. p. 128°, is produced, whilst, in the absence of iodine, a *dibromide*, m. p. 81°, is obtained, which liberates iodine from alcoholic potassium iodide, thus showing that the bromine atoms are attached to adjacent carbon atoms When a solution of this dibromide in acetone is oxidised with potassium permanganate in presence of acetic acid, small quantities of a *substance*, m. p. 131°, are produced, which contains halogen, but does not liberate iodine from alcoholic potassium iodide.

Ethyl α-cyanocinnamylideneacetate reacts readily with organic magnesium compounds with production of quantitative yields of $a\delta$-additive compounds. When this ester (1 mol.) is treated with magnesium ethyl bromide ($2\frac{1}{2}$ mols.) and the product is decomposed with hydrochloric acid, *ethyl α-cyano-δ-phenyl-β-ethyl-Δ^{γ}-pentenoate*, $CHPh{:}CH \cdot CHEt \cdot CH(CN) \cdot CO_2Et$, b. p. 220°/20 mm., is obtained as a yellow oil ; on hydrolysis with potassium hydroxide, the *potassium* salt is obtained, from which the *acid* separates on the addition of hydrochloric acid as an uncrystallisable oil. On heating this acid with alcoholic potassium hydroxide for two days, it is converted into *δ-phenyl-β-ethylallylmalonamic acid*,

$$CHPh{:}CH \cdot CHEt \cdot CH(CO \cdot NH_2) \cdot CO_2Et,$$

m. p. 165°, which, when heated above its m. p., yields *δ-phenyl-β-ethyl-Δ^{γ}-pentenoamide*, $CHPh{:}CH \cdot CHEt \cdot CH_2 \cdot CO \cdot NH_2$, m. p. 101°, which forms slender needles.

Ethyl α-cyanocinnamylideneacetate reacts with magnesium phenyl bromide to form *ethyl α-cyano-$\beta\delta$-diphenyl-Δ^{γ}-pentenoate*,

$$CHPh\!:\!CH\cdot CHPh\cdot CH(CN)\cdot CO_2Et,$$

b. p. 263°/18 mm.

Both α-cyano- and α-methyl-cinnamylideneacetic acids react readily with potassium hydrogen sulphite, yielding colourless, additive compounds which could not be isolated. E. G.

Unsaturated Compounds. VIII. Addition of Hydroxylamine to Unsaturated Acids containing Conjugate Double Linkings. THEODOR POSNER and KARL ROHDE (*Ber.*, 1910, **43**, 2665—2676. Compare Abstr., 1909, i, 583, 649; Riedel and Schulz, *ibid.*, i, 581).—In further proof of the constitution of β-benzoylamino-β-styrylpropionic [β-benzoylamino-δ-phenyl-Δ^{γ}-pentenoic] acid is adduced the fact that on oxidation benzoylaspartic acid is formed. Although β-benzoylamino-δ-phenyl-Δ^{γ}-pentenoic acid and its ester contain olefinic linkings, it has not been found possible to form additive compounds with hydroxylamine or bromine. The addition of hydroxylamine to styrylacrylic acid proceeds slowly, for example, 240 hours' boiling of the solution is required, whereas with cinnamic acid five hours is sufficient.

The addition of hydroxylamine to sorbic, piperic, and α-phenylstyrylacrylic acids and their esters has been studied. The compounds combine with hydroxylamine (compare Riedel and Schulz, *loc. cit.*): sorbic acid at much the same rate as styrylacrylic acid, piperic acid much less readily, as also α-phenylstyrylacrylic acid and all α-alkylated unsaturated acids.

β-Amino-δ-phenyl-Δ^{γ}-pentenoic acid can be obtained by prolonged boiling of β-hydroxylamino-δ-phenyl-Δ^{γ}-pentenohydroxamoxime hydrate (Abstr., 1909, i, 649) with methyl alcohol. It has not been found possible to prepare Riedel and Schulz's β-hydroxylamino-δ-phenyl-Δ^{γ}-pentenohydroxamic acid by the method they give; the product formed under these conditions is *styrylacrylhydroxamic acid*,

$$CHPh\!:\!CH\cdot CH\!:\!CH\cdot C(OH)\!:\!N\cdot OH,$$

m. p. 146°.

Methyl sorbate, $CHMe\!:\!CH\cdot CH\!:\!CH\cdot CO_2Me$, is a colourless liquid with a pleasant odour, and has b. p. 180°/759 mm. The ester reacts with a cold solution of hydroxylamine in methyl alcohol during the course of a week, yielding an oil which is probably *β-hydroxylaminohydrosorbhydroxamoxine hydroxide*. *Aminohydrosorbic acid* (*β-amino-Δ^{γ}-hexenoic acid*) is formed when the above hydroxide is boiled with methyl alcohol, or when a mixture of the methyl ester and hydroxylamine is boiled for ten hours with methyl alcohol. The same product is also formed when free sorbic acid is used, but the boiling must then be continued for 240 hours; it is an oil, and yields a *benzoyl* derivative, $CHMe\!:\!CH\cdot CH(NH\cdot COPh)\cdot CH_2\cdot CO_2H$, which crystallises from alcohol, and has m. p. 152°.

Methyl piperate, $CH_2O_2\!:\!C_6H_3\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot CO_2Me$, is deposited from methyl alcohol in glistening crystals, m. p. 146°, and reacts with a hot methyl-alcoholic solution of hydroxylamine, yielding *β-amino-α-hydropiperic acid* (*β-amino-δ-3 : 4-methylenedioxyphenyl-Δ^{γ}-pentenoic*

acid), $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H$, which crystallises from water in colourless needles, m. p. 231° (decomp.). A small amount of the same product is also formed when sorbic acid itself is used; it yields a *benzoyl* derivative, $C_{19}H_{17}O_5N$, m. p. 188°, and reacts with potassium cyanate, forming *β-carbamido-α-hydropiperic acid*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH(NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CO_2H$, as glistening crystals, m. p. 211°. The carbamido-acid, when heated at 215°, yields 3 : 4-*methylenedioxystyryldihydrouracil*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{<}{\begin{matrix}CH_2{\cdot}CO\\NH{-}CO\end{matrix}}{>}NH,$$

as a yellow, crystalline powder, m. p. 224°.

Methyl α-phenylstyrylacrylate, $CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CO_2Me$, forms yellow crystals, m. p. 79—80°, and when boiled for several days with hydroxylamine and methyl alcohol yields *β-amino-αδ-diphenyl-*Δ^{γ}*-pentenoic acid*, $CHPh{:}CH{\cdot}CH(NH_2){\cdot}CHPh{\cdot}CO_2H$, which crystallises from water in colourless needles, m. p. 200° (decomp.). The *benzoyl* derivative, $C_{24}H_{21}O_3N$, forms colourless, glistening crystals, m. p. 222·5°, and *β-carbamido-αδ-diphenyl-*Δ^{γ}*-pentenoic acid*,

$$CHPh{:}CH{\cdot}CH(NH{\cdot}CO{\cdot}NH_2){\cdot}CHPh{\cdot}CO_2H,$$

colourless, glistening needles, m. p. 197°; the corresponding 5-*phenyl-4-styryldihydrouracil*, $CHPh{:}CH{\cdot}CH{<}{\begin{matrix}CHPh{\cdot}CO\\NH{-\!-}CO\end{matrix}}{>}NH$, forms a pale yellow powder, m. p. 212·5°, after softening at 192°.

When cinnamylidenemalonic acid is heated with methyl alcohol and hydroxylamine, carbon dioxide is evolved, and β-amino-δ-phenyl-Δ^{γ}-pentenoic acid is formed, whereas the corresponding methyl ester reacts with a methyl-alcoholic solution of hydroxylamine at 0°, yielding a crystalline product, m. p. 72°, which is probably a hydroxylamino-hydroxamoxime hydroxide. J. J. S.

A New Step in the Reduction of the Nitro-group. III. GUSTAV HELLER and FRIEDRICH FRANTZ (*Ber.*, 1910, **43**, 2892—2899. Compare Abstr., 1906, i, 585; 1908, i, 208).—Since in the numerous cases examined it has not been possible to obtain the compound containing a dihydroxylamine group, which is the first product of the reduction of *o*-nitromandelonitrile, substituted mandelonitriles have now been investigated. Of these, 5-chloro-2-nitromandelonitrile does not yield the characteristic molecular compound in solid form, although its presence in the liquid can be shown by the production of 5-chloroisatin on acetylation. In the case of 5-bromo-2-nitromandelonitrile, the desired substance is obtainable in the form of its hydrochloride, although with a poor yield, and its reactions correspond in all respects with the observations previously recorded. A further proof of the existence of the combination of di- and mono-hydroxylamine compounds follows from the fact that solutions of the above hydrochloride when kept deposit 5-bromo-2-nitrosomandelonitrile, so that evidently no tendency to the formation of an azoxy-compound exists.

5-*Chloro-2-nitromandelonitrile*, $C_8H_5O_3N_2Cl$, is prepared by adding a concentrated, aqueous solution of potassium cyanide to a solution of 5-chloro-2-nitrobenzaldehyde (Einhorn and Eichengrün, Abstr., 1891, 1098) in glacial acetic acid, or by adding the aldehyde to twice its weight of anhydrous hydrocyanic acid. It forms rosettes

of needles, m. p. 85°, and also large prisms containing chloroform of crystallisation, m. p. 64—66°.

5-*Chloro*-2-*nitromandelic acid*, $C_8H_6O_5NCl$, m. p. 134°, is obtained by evaporating the nitrile with twenty times its weight of hydrochloric acid almost to dryness. The *methyl* ester, $C_9H_8O_5NCl$, has m. p. 87—88°. With alcoholic ammonia, 5-chloro-2-nitromandelonitrile yields the *ammonium* salt of 5-*chloro*-2-*nitrosobenzoic acid*, which may be obtained from it by the action of dilute hydrochloric acid. The free acid crystallises in colourless needles, which become coloured towards 170° and melt at 179°. After reduction with zinc and acetic acid no precipitate was observed, but on addition of hydrochloric acid and acetic anhydride a dark-coloured oil separated, and the solution when kept yielded 5-chloroisatin. The oil was insoluble in cold sodium hydroxide, and therefore was not 5-chloro-*N*-acetoxyisatin.

5-*Bromo*-2-*nitromandelonitrile*, prepared from 5-bromo-2-nitrobenzaldehyde, has m. p. 81°. When it is reduced with zinc and acetic acid in an atmosphere of hydrogen, the liquid being cooled with water and well stirred, the molecular compound of 5-*bromo*-2-*mono*- and 5-*bromo*-2-*di-hydroxylaminomandelonitrile hydrochloride*, $C_{16}H_{16}O_5N_4Cl_2Br_2$, separates. After purification by precipitation with concentrated hydrochloric acid from solution in weaker acid, it crystallises in a mass of colourless, crooked needles, which become coloured at 130° and decompose towards 145°. The free compound can also be isolated. On keeping, an aqueous solution of the hydrochloride deposits a brown precipitate, which, when saponified with dilute sodium hydroxide, yields bromoanthroxanic acid and bromoisatin. These substances are obtained directly by heating the salt with concentrated hydrochloric acid. 5-*Bromoisatin*, $C_8H_4O_2NBr$, forms yellow needles, m. p. 255°. 5-*Bromoanthroxanic acid*, $C_8H_4O_3NBr$, crystallises in colourless needles. It melts at 202—203°, with evolution of gas and partial sublimation; the yellow residue darkens on further heating, and melts towards 253° with evolution of gas. Bromoanthroxanic acid is reduced by ammoniacal ferrous sulphate, and on acidification 5-bromoisatin is precipitated. The hydrochloride of the molecular compound yields on treatment with dilute sodium hydroxide a colourless *compound*, m. p. 186—187°, and an aminocarboxylic acid, probably 5-*bromo*-2-*amino-mandelic acid*, crystallising in colourless needles, which become coloured towards 230°. Acetylation of the molecular compound in presence of an excess of hydrochloric acid gives rise to 5-bromo-1-acetoxyisatin. Phenylhydrazine reacts with the hydrochloride, yielding 5-bromo-1-hydroxyisatinphenylhydrazone and 5-*bromo-isatin*-2-*phenylhydrazone*, $C_{14}H_{10}ON_3Br$, which forms dark red crystals, m. p. 242—243°.

5-*Bromo*-2-*nitrosomandelonitrile*, $C_8H_5O_2N_2Br$, which can be obtained (in addition to 5-bromoisatin) from the filtrate from the molecular compound in the preparation of the latter, crystallises in compact, colourless prisms, m. p. 225—226°. On hydrolysis it yields 5-bromoanthroxanic acid. R. V. S.

Action of Amines on Phthalic Acid. VII. J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1910, **32**, 1319—1330).—In continuation of the work on the interaction of amines with phthalic

acid and its derivatives (Abstr., 1907, i, 692, 1044; 1909, i, 28, 798, 909; this vol., i, 263), a study has been made of phthalamic acids containing one or more chlorine atoms or nitro-groups in the benzene nucleus.

Di-m-*toluidine* and *di*-p *chloroaniline* 3 : 6-*dichlorophthalates*, m. p. 176° and 215° respectively, form pale yellow crystals. An improved method is described for the preparation of 3 : 6-dichlorophthalanilic acid and its anil. The anil has m. p. 201°, and not 191° as stated by Graebe (Abstr., 1900, i, 547). The acid is not affected by solutions of amines in benzene, but is readily converted into the anil by the action of 50% alcohol. This dehydrating action of alcohol has been discussed by Tingle and Rolker (Abstr., 1909, i, 29).

Tetrachlorophthal-o-toluidic acid, $C_6H_4Me\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 218—220°, obtained by the action of *o*-toluidine on tetrachlorophthalic acid or anhydride, forms white, lustrous crystals.

Tetrachlorophthalanilic acid, $NHPh\cdot CO\cdot C_6Cl_4\cdot CO_2H$, m. p. 266°, obtained by boiling tetrachlorophthalanil (Graebe and Buenzod, Abstr., 1899, i, 763) with solution of potassium hydroxide or by the action of aniline on tetrachlorophthalic anhydride, forms white crystals; its *sodium* and *potassium* salts are colloidal, and yield soapy solutions. *Tetrachlorophthalo-β-naphthylamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot C_6Cl_4\cdot CO_2H$, m. p. 287°, forms white crystals, and yields colloidal *sodium* and *potassium* salts. When the acid is heated for ten minutes at 260—270°, it is converted into the *β-naphthylimide*, $C_6Cl_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N\cdot C_{10}H_7$, m. p. 287°, which is a white, crystalline substance.

When 3-nitrophthalanilic acid, $NHPh\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H$, is heated at 100° with 50% alcohol, it is slowly transformed into a 3-*nitrophthalodianilide*, m. p. 233—234°, which appears to be isomeric with that obtained by Chambers (Abstr., 1903, i, 699) of m. p. 211—212°. 3-*Nitrophthalo-β-naphthylamic acid*,

$$C_{10}H_7\cdot NH\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H,$$

m. p. 201—202°, obtained by the action of β-naphthylamine on 3-nitrophthalic anhydride, forms light yellow crystals.

4-Nitrophthalanilic acid, obtained by heating the anil (Graebe and Buenzod, *loc. cit.*) with solution of potassium hydroxide or by treating aniline with 4-nitrophthalic anhydride, has m. p. 192°, and not 181° as stated by Bogert (Abstr., 1902, i, 98). The anil has m. p. 200—201° (Bogert gives 194°). When 4-nitrophthalanilic acid is heated at 100° with 50% alcohol, it is partly transformed into the anil; in presence of aniline the same product is obtained, together with a small quantity of a *compound*, m. p. 199—200°, which is probably 4-nitrophthalodianilide, $NO_2\cdot C_6H_3(CO\cdot NHPh)_2$.

On comparing the results of the transformation experiments with 3- and 4-nitrophthalanilic acids, it is evident that the approximation of negative groups ($CO_2H:CO_2H:NO_2 = 1:2:3$) inhibits the formation of the anil and greatly favours that of the dianilide, whereas the reverse is the case when the nitro-group is in the 4-position. 4-*Nitrophthalo-β-naphthylamic acid*, $C_{10}H_7\cdot NH\cdot CO\cdot C_6H_3(NO_2)\cdot CO_2H$, m. p. 202—204°, prepared by the action of β naphthylamine on 4-nitrophthalic anhydride, forms pale yellow crystals.

Camphoro-β-naphthylamic acid, $C_{10}H_7 \cdot NH \cdot CO \cdot C_8H_{14} \cdot CO_2H$, m. p. 220—221°, obtained by the action of β-naphthylamine on camphoric anhydride, and camphoranilic acid (Auwers, Abstr., 1900, i, 85) are not affected by prolonged heating with amines or with 50% alcohol.

E. G.

Synthesis of Ethyl *cyclo*Butanehexacarboxylate. YUGI SHIBATA (*Ber.*, 1910, **43**, 2619—2622).—*Ethyl* cyclo*butanehexacarboxylate*, $(CO_2Et)_2C<\begin{matrix}C(CO_2Et)_2\\CH(CO_2Et)\end{matrix}>CH \cdot CO_2Et$, can be synthesised by the action of the disodium derivative of ethyl ethanetetracarboxylate (Bischoff and Rach, Abstr., 1885, 244) on ethyl dibromosuccinate (Gorodetzky, Abstr., 1888, 820) in the presence of dry ether at 0° and with vigorous automatic stirring. It crystallises from alcohol in large, monoclinic plates [$a:b:c = 1.565:1:1.542$; $\beta = 131°32'$], m. p. 80°. Unaltered ethyl ethanetetracarboxylate is deposited with the *cyclo*butane derivative, but can be removed mechanically, as it forms large, needle-shaped crystals.

An oily by-product formed during the condensation is Bischoff's ethyl ethylenetetracarboxylate, $C(CO_2Et)_2:C(CO_2Et)_2$. The condensation does not take place when the reagents are heated in sealed tubes at 120—130°, and the same products are formed when ethyl *iso*dibromosuccinate is used.

J. J. S.

Rotatory Power of Usnic Acid and other Lichen Derivatives. III. HEINRICH SALKOWSKI (*Annalen*, 1910, **377**, 123—126. Compare Abstr., 1901, i, 152; 1902, i, 228).—The values for $[\alpha]_D^t$ for the following substances are given: *d*-Usnic acid (from nineteen species of lichens), +461·9° to +521·9°; *l*-usnic acid (from thirteen species), −455·9° to −496·8°; kamschadalic acid, +26·42°; lepranthin, +70·5°; pleopsidic acid, −66·15°; protolichenosteric acid, +12·1°.

Barbatic acid, lecanarolic acid, and salazinic acid appear to be inactive.

In most cases chloroform solutions were used.

Gymnogrammen from *Gymnogramme chrysophylla* has an orange colour, m. p. 159°, and $[\alpha]_D^{18}$ +12°.

J. J. S.

Ethyl Tannate. RODGER J. MANNING (*J. Amer. Chem. Soc.*, 1910, **32**, 1312—1319).—The composition of gallotannic acid has hitherto been uncertain, owing to the fact that crystalline derivatives were not known, and the substance was therefore difficult to purify. The ethyl ester has now been prepared in two crystalline forms with different amounts of water of crystallisation.

On treating an alcoholic solution of gallotannic acid with dry hydrogen chloride, *ethyl gallotannate*, $C_{51}H_{52}O_{26},5H_2O$, m. p. 157°, is obtained in the form of nodules of pale yellow, lustrous crystals. When hydrolysed with dilute hydrochloric acid or dilute potassium hydroxide, it yields ethyl alcohol, dextrose, and gallic acid. Estimations of the gallic acid and dextrose, and determinations of the molecular

weight by the ebullioscopic method have shown that ethyl gallotannate has the composition $C_{41}H_{27}O_{21}(OEt)_5,5H_2O$, and that it is a glucoside in which one formula weight of dextrose and five formula weights of gallic acid are represented in one molecule of the ester. Gallotannic acid is therefore represented by the formula $C_{41}H_{27}O_{21}(OH)_5$.

The ester was synthesised by treating a mixture of ethyl gallate and dextrose with phosphoryl chloride.

If a saturated solution of the ester is allowed to evaporate at the ordinary temperature, large, pale brown crystals are obtained of the composition $C_{51}H_{52}O_{26},15H_2O$, m. p. 132°. E. G.

Theory of the Phenomena of Halochromy. I. Additive Compounds of Tin Halogenides and Carbonyl Compounds. PAUL PFEIFFER [with O. HALPERIN, E. PROS, and V. SCHWARZKOPF] (*Annalen*, 1910, **376**, 285—310).—The first step in the elucidation of the constitution of the coloured additive compounds of organic substances and metallic salts and acids, and therewith the nature of the phenomenon of halochromy, must be a systematic examination of the additive capacity of simply constituted substances. Since halochromy is most frequently observed in connexion with carbonyl compounds, these have been selected as the organic components; the inorganic are tin tetrachloride and tetrabromide, which have the property of forming well-characterised molecular compounds of simple composition.

The additive compound is obtained by bringing the tin halogenide and the carbonyl compound (aldehyde, ketone, acid, ester, or amide, containing generally the benzoyl or cinnamoyl group; acid chlorides do not form additive compounds) together in anhydrous ether, benzene, or chloroform; in the case of liquid esters, a solvent is dispensed with. In this way have been prepared the following colourless compounds: $SnCl_4,2PhCHO$, m. p. 187—189°; $SnBr_4,2PhCHO$, m. p. 127—128°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CHO$, m. p. 225—230°; $SnBr_4,2CHPh{\cdot}CH{:}CH{\cdot}CHO$, m. p. 195°; $SnCl_4,2(p)OH{\cdot}C_6H_4{\cdot}CHO$, m. p. 185°; $SnCl_4,2(p)OMe{\cdot}C_6H_4{\cdot}CHO$, m. p. 158°; $SnCl_4,2COPhMe$, m. p. 131—133°; $SnCl_4,2Ph{\cdot}CO_2Et$, m. p. 40°; $SnCl_4,2(p)C_6H_4Me{\cdot}CO_2Et$; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO_2Et$, m. p. 134°; $SnBr_4,2(o)OH{\cdot}C_6H_4{\cdot}CO_2Me,2H_2O$, m. p. 67—68°; $SnCl_4,2Ph{\cdot}CO_2H$, m. p. about 90°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO_2H$, m. p. 85—112°; $SnCl_4,2Ph{\cdot}CO{\cdot}NH_2$, m. p. about 227°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}CO{\cdot}NH_2$, m. p. 238—239°; $SnCl_4,2(o)OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 205°; and also the following, which are yellow or yellowish: $SnCl_4,2C_4OH_3{\cdot}CHO$, unstable; $SnBr_4,2(p)OH{\cdot}C_6H_4{\cdot}CHO$, m. p. 154°; $SnCl_4,2CHPh{\cdot}CH{:}CH{\cdot}COMe$, m. p. 120°. All these compounds are decomposed by water, and contain 1 molecule of the inorganic to 2 of the organic component. Their composition may be represented, therefore, by the general expression $SnX_4,2R{\cdot}CO{\cdot}A$, where X is chlorine or bromine, R is Ph, ${\cdot}C_6H_4{\cdot}OH$, ${\cdot}C_6H_4{\cdot}OMe$, ${\cdot}CHPh{:}CH$, or ${\cdot}C_4OH_3$, and A is H, Me,

OH, OEt, or NH_2. The common constituent of all these compounds is the carbonyl group, which therefore is the means by which the organic and the inorganic components are linked. The co-ordination number of tin is six. Moreover, additive compounds of the tin series are formed, almost without exception, extra-molecularly, not intra-molecularly. Therefore the two organic molecules of the additive compound probably occupy the two free co-ordination positions of the SnX_4 molecule, being linked by the oxygen, since tin has a much greater affinity for oxygen than for carbon. These views lead to the constitution $X_4Sn{<}^{\cdot\cdot O:CRA}_{\cdot\cdot O:CRA}$ for the preceding additive compounds.

These views, in conjunction with Thiele's theory, are utilised by the author to explain the facts that in a compound containing an unsaturated group the saturation of this group tends to diminish the colour intensity, whilst by the formation of a molecular additive compound colour is produced or intensified. For example, a substance, $\substack{R\\R}{>}C:O$, in virtue of the residual affinities of the carbon and oxygen atoms, is converted by the addition of Y·Y into a more saturated system, $\substack{R\\R}{>}CY\cdot OY$, with a corresponding diminution or loss of colour; this is not surprising, because, according to modern views, the colour of purely organic substances is due primarily to the presence of unsaturated groups. When, however, an extramolecular additive compound, such as those above, is formed by a neutralisation of the residual affinity of the oxygen atom only, the unsaturated carbon atom acquires a more pronounced unsaturated character, approximating to that of tervalent carbon, and therefore may be regarded as a specific chromophore, and the additive compound, under suitable circumstances, may be coloured or exhibit halochromy.

In the author's opinion the action of catalysts in hydrolysis, esterification, ketone-synthesis, etc., may be explained by the initial formation of a molecular compound of the catalyst and the organic substance at its carbonyl oxygen atom. C. S.

Action of Chloride of Sulphur and of Sulphuryl Chloride on Piperonal. KARL WEISSE (*Ber.*, 1910, **43**, 2605—2606. Compare D.R.-P. 165727).—Piperonal reacts to only a slight extent when distilled with sulphuryl chloride, but when a mixture of the two compounds is kept at the ordinary temperature for two days a good yield of *chloropiperonal*, $C_8H_5O_3Cl$, is obtained; it crystallises from alcohol in brilliant needles, m. p. 114—115°.

When this chloro-derivative is heated with chloride of sulphur at 150° for an hour, and then at 130° for three hours, a resinous product is obtained, which loses carbon dioxide when heated, forming *chloroprotocatechualdehyde*, $C_7H_5O_3Cl$, m. p. 211°.

Chloroprotocatechualdehyde reacts with an alcoholic potassium hydroxide solution of ethyl chlorocarbonate, yielding the *ethyl carbonate* derivative, $C_{10}H_9O_5Cl$, which crystallises from water in glistening plates, m. p. 135°. J. J. S.

Condensation Products of *o*-Phthalaldehyde. III. JOHANNES THIELE and ERNST WEITZ (*Annalen*, 1910, **377**, 1—22. Compare Thiele and Falk, Abstr., 1906, i, 750; Thiele and Schneider, Abstr., 1909, i, 929).—Ketones with the grouping $CH_3\cdot CO\cdot CH_2$ can react with *o*-phthalaldehyde in two distinct ways: (*a*) formation of a hydrindone derivative, as in the case of acetone or acetophenone; (*b*) formation of a benzo*cyclo*heptadienone, as in the case of diethyl ketone.

It is shown that methyl ketones which contain a normal carbon chain react according to the latter scheme; thus methyl ethyl, methyl propyl, and methyl *n*-butyl ketones yield respectively methyl-, ethyl-, and propyl-benzo*cyclo*heptadienones, $C_6H_4<\substack{CH:CR\\CH:CH}>CO$. Naphthalene derivatives do not appear to be formed, but small amounts of acylhydrindones can be detected among the condensation products. Methyl *iso*butyl ketone yields as chief condensation product *iso*valerylhydrindone, and practically no *iso*propylbenzo*cyclo*heptadienone. Methyl *iso*propyl ketone yields isobutyrylhydrindone, as there is no methylene group present capable of yielding a benzo*cyclo*heptadienone derivative.

Phthalaldehyde also condenses readily with nitromethane, yielding nitrohydrindone, which reacts in the enolic form, nitrohydroxyhydrindene, as it yields an acetyl derivative and a methyl ether. Its constitution has been determined by conversion into Gabriel's aminohydrindone.

*Benzo*cyclo*heptadienone*, $C_6H_4<\substack{CH:CH\\CH:CH}>CO$, prepared by heating the carboxylic acid (Abstr., 1909, i, 930) with 0·5% hydrochloric acid at 200° for four to five hours, crystallises from light petroleum in pale yellow plates, m. p. 66—67°, and does not react with phenylhydrazine or hydroxylamine. The *dibromide*, $C_{11}H_{18}OBr_2$, forms colourless needles, m. p. 204°. *Dimethylbenzo*cyclo*heptadienone*,

$$C_6H_4<\substack{CH:CMe\\CH:CMe}>CO,$$

prepared from diethyl ketone and phthalaldehyde in the presence of methyl-alcoholic potassium hydroxide solution, crystallises from dilute alcohol in colourless plates, m. p. 85°; *diphenylbenzo*cyclo*heptadienone*, $C_{23}H_{16}O$, obtained when dibenzyl ketone is used, crystallises in pale yellow prisms, m. p. 118·5°, and does not yield a dibromide; *methylbenzo*cyclo*heptadienone*, $C_{12}H_{10}O$, crystallises from light petroleum (40—70°) in felted needles, m. p. 61°; the corresponding *ethyl* derivative, $C_{13}H_{12}O$, has m. p. 42—43°, and the n-*propyl* derivative, $C_{14}H_{14}O$, has b. p. 188°/13 mm., and solidifies when kept in a freezing mixture.

*Diphenylbenzo*cyclo*heptanone*, $C_6H_4<\substack{CH_2\cdot CHPh\\CH_2\cdot CHPh}>CO$, prepared by reducing the corresponding dienone with sodium amalgam and alcohol in the presence of acetic acid, crystallises from 75% alcohol in colourless needles, m. p. 158°. The ketone does not react with phenylhydrazine or semicarbazide, but with magnesium methyl iodide yields *diphenylmethylbenzo*cyclo*heptanol*, $C_6H_4<\substack{CH_2\cdot CHPh\\CH_2\cdot CHPh}>CMe\cdot OH$, which

forms colourless crystals, m. p. 211°, and is stable towards permanganate.

Dimethylbenzocycloheptanol, $C_6H_4<\begin{smallmatrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{smallmatrix}>CH\cdot OH$, obtained by reducing the corresponding dienone, crystallises from dilute alcohol in colourless needles, m. p. 123—124°, and yields an *acetyl* derivative, m. p. 141°. *Diphenylbenzocycloheptanol*, $C_{23}H_{22}O$, forms colourless plates, m. p. 160°. *Benzocycloheptanol*, $C_6H_4<\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}>CH\cdot OH$, prepared from benzo*cyclo*heptadienone, has m. p. about 80°.

iso*Valerylhydrindone* (*1-hydroxy-2-*iso*valerylhydrindene*),

$$C_6H_4<\begin{smallmatrix}C(OH)\\CH_2\end{smallmatrix}>C\cdot CO\cdot CH_2\cdot CMe_2,$$

crystallises from methyl alcohol in needles, soluble in alkalis, and gives a red to reddish-violet coloration with ferric chloride. When a small amount of alkali is used in the condensation, much phenylnaphthylene ketone is formed. iso*Butyrylhydrindone* (*1-hydroxy-2-*iso*butyrylhydrindene*), $C_6H_4<\begin{smallmatrix}C(OH)\\CH_2\end{smallmatrix}>C\cdot CO\cdot CHMe_2$, has b. p. 170—174°/13—14 mm., and m. p. 35—36°.

2-Nitro-1-hydrindone (*2-nitroindenol*), $C_6H_4<\begin{smallmatrix}C(OH)\\CH_2\end{smallmatrix}>C\cdot NO_2$, crystallises from light petroleum (100°) in slender, sulphur-yellow needles, m. p. about 117° (decomp.). It dissolves in alkali hydroxide solutions and is decomposed when boiled with water. The *acetyl* derivative, $C_{11}H_9O_4N$, crystallises in slender, yellow needles, turns dark coloured at 108—109°, melts and decomposes above 120°, and yields a *dibromide*, $C_{11}H_9O_4NBr_2$, in the form of colourless, compact crystals, m. p. 136°. The *methyl ether* of the nitro-derivative, $C_9H_9O_3N$, is obtained readily from the acetyl derivative by the action of methyl alcohol and hydrogen chloride; it crystallises in pale yellow plates, m. p. 83°.

Hydrobenzoin-o-dialdehyde, $CHO\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot C_6H_4\cdot CHO$, prepared by reducing phthalaldehyde with zinc dust in the presence of alcohol and glacial acetic acid at the ordinary temperature, crystallises from alcohol in minute needles, m. p. 176—177°. Its solution in concentrated sulphuric acid has an intense yellow colour with a greenish-yellow fluorescence. Its *phenylhydrazone*, $C_{28}H_{26}O_2N_4$, crystallises from aniline, and has m. p. above 260°. When oxidised with nitric acid the dialdehyde yields hydrodiphthalyl (compare Hasselbach, Abstr., 1888, 485), but with alkaline permanganate yields benzil-*o*-dicarboxylic acid (Graebe, Abstr., 1888, 1095; 1890, 989). Concentrated sulphuric acid reacts with a solution of the dialdehyde in glacial acetic acid, yielding *2-o-aldehydophenyl-3-indone*, $C_6H_4<\begin{smallmatrix}CO\\CH\end{smallmatrix}>C\cdot C_6H_4\cdot CHO$, which crystallises from alcohol in brilliant, orange-red needles, m. p. 141°. An amorphous by-product is formed at the same time, and the amount of this increases if the reaction mixture is heated for some time. The indone derivative reduces ammoniacal silver nitrate solution and also alkaline permanganate, and yields a *dibromide*, $C_{16}H_{10}O_2Br_2$, m. p. above 240°. A small amount of this indone is formed in the preparation of phthaldehyde.

J. J. S.

Synthesis of Ketones in the Tetrahydroaromatic Series. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1910, **151**, 758—759).—This paper contains an account of further applications of the general reaction already described (this vol., i, 322) to *cyclo*hexene. By treating this hydrocarbon with *n*-butyryl chloride in presence of aluminium chloride, a condensation product is obtained, which loses hydrogen chloride when heated with diethylamine, forming n-*butyryl*cyclo*hexene*, $C_3H_7\cdot CO\cdot C_6H_9$, b. p. 225—226°, 113—114°/7 mm.; the *semicarbazone* has m. p. 171°. iso*Valeryl*cyclo*hexene* has b. p. 233°, 128—130°/7 mm.; the *semicarbazone* has m. p. 180°. *Heptoyl*cyclo*hexene* has b. p. 274—275°, 140—141°/5 mm.; the *semicarbazone* has m. p. 145°. *Lauryl*cyclo*hexene*, b. p. 342—343°, 209—211°/6 mm., forms a *semicarbazone*, m. p. 125°.

The foregoing ketones may be utilised for the production of hexahydroaromatic ketones, the reduction being effected by catalytic hydrogenation in presence of reduced nickel.

By condensing tetrahydroacetophenone with ethyl chloroacetate in presence of sodium ethoxide, *ethyl methyl*cyclo*hexenylglycidate*, $O<\begin{matrix}CMe\cdot C_6H_9\\ CH\cdot CO_2Et\end{matrix}$, has been obtained. This substance has b. p. 145—148°/14 mm., and on hydrolysis gives an unstable acid, which loses carbon dioxide when heated in a vacuum, forming *tetrahydroatropaldehyde*, $C_6H_9\cdot CHMe\cdot CHO$, b. p. 90—93°/15 mm. W. O. W.

The Pinacone Transformation in the Case of Cyclic Compounds. I. HANS MEERWEIN and WALTER UNKEL (*Annalen*, 1910, **376**, 152—163).—1-*iso*Propyl*cyclo*pentane-1 : α-diol,

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CMe_2\cdot OH,$$

prepared by the action of magnesium methyl iodide on methyl α-hydroxy*cyclo*pentanecarboxylate, readily undergoes the pinacone transformation when heated with dilute sulphuric or oxalic acid. An intermediate product is probably the oxide, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CMe_2\\ O\end{matrix}$, but the final product isolated is 1 : 1-dimethyl*cyclo*hexan-6-one, the constitution of which was determined by oxidation to αα-dimethyladipic acid by means of nitric acid. The reaction (cyclic pinacone transformation) consists in the conversion of a 5-carbon into a 6-carbon ring, and is of interest as bearing on certain transformations in the terpene series.

Reactions of the same type are the conversion of pulegenic acid (*iso*propylidenemethyl*cyclo*pentanecarboxylic acid) into pulenone (1 : 4 : 4-trimethyl*cyclo*hexan-5-one) (compare Wallach, Abstr., 1904, i, 74); also the conversion of di*cyclo*pentanepinacone into 1 : 1-tetramethylene*cyclo*hexan-2-one (Meiser, Abstr., 1899, i, 742), and the transformation of fluorenone into a phenanthrene derivative when reduced with zinc and acetyl chloride, a pinacone being the intermediate product, which has not been isolated :

$$\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CO \longrightarrow \begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix} \longrightarrow \begin{matrix}C_6H_4\cdot CO\\ C_6H_4\cdot C\end{matrix}<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$$

(compare Klinger and Lonnes, Abstr., 1896, i, 691).

Methyl cyclo*pentan*-1-*ol*-1-*carboxylate*,

$$\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!>C(OH)\cdot CO_2Me,$$

is readily prepared from the acid (Gärtner, Abstr., 1893, i, 557) by the usual method. It has b. p. 87°/23 mm., or 84°/16 mm. 1-iso*Propyl*cyclo*pentane*-1 : *a-diol*, $C_8H_{16}O_2$, crystallises from light petroleum in glistening, colourless prisms, m. p. 62°, and b. p. 105—110°/15 mm.

1 : 1-*Dimethyl*cyclo*hexan*-6-*one*, $CH_2<\begin{matrix} CH_2-CO \\ CH_2\cdot CH_2 \end{matrix}>CMe_2$, is a colourless oil, and yields a *semicarbazone*, $C_9H_{17}ON_3$, which crystallises in large, flat needles, m. p. 196—197°. The pure ketone, prepared by hydrolysing the semicarbazone with 10% sulphuric acid, has b. p. 59·5°/14 mm. or 170·2—170·4°/758 mm., D^{20} 0·9194, and n_D^{20} 1·44744, and has an odour of camphor and menthone.

A small amount of an unsaturated hydrocarbon accompanies the crude ketone. J. J. S.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds Containing Alkyloxy-groups. Grace Potter Reynolds (*Amer. Chem. J.*, 1910, **44**, 305—331).—The reactions between organic magnesium compounds and unsaturated compounds have been studied by Kohler (Abstr., 1905, i, 208; 1907, i, 139, 1050) with special reference to the effect of hydrocarbon residues in substances containing the chain C:C·C:O, as the result of which it is possible to predict the mode of addition of a magnesium compound to such a substance. It has also been shown that in the reactions with ethyl α-cyanocinnamate (Abstr., 1905, i, 347) and ethyl benzylidenemalonate (Abstr., 1905, i, 700) the presence of the cyano- and carbethoxy-groups in the α-position prevents the replacement of the alkyloxy-group, and therefore only αδ-additive products are obtained. In continuation of this work, an investigation has been made of the influence of alkyloxy-groups on the mode of addition. An attempt has been made to use the Grignard reagent for the study of keto-enol-tautomerism, but it has been found to be unsuitable for the purpose.

Magnesium methyl iodide reacts instantaneously with phenyl formylethyl ketone when dissolved in ethyl ether, but does not react with it in an amyl ether solution, and it is therefore evident that the method cannot be used for the estimation of the hydroxyl group in this ketone (compare Hibbert and Sudborough, Trans., 1904, **85**, 933, and Zerewitinoff, Abstr., 1907, ii, 509).

Ethyl hydroxymethylenemalonate and phenyl formylethyl ketone were selected for the experiments to ascertain whether the nature of the products obtained in the Grignard reaction can serve for the estimation of the relative amounts of ketonic and enolic modifications. Magnesium phenyl bromide reacts with ethyl hydroxymethylenemalonate to form a product, which, when decomposed in the usual way, yields ethyl benzylidenemalonate. Magnesium ethyl bromide also reacts with ethyl hydroxymethylenemalonate, but the product could not be identified.

Ethyl α-phenylpropylmalonate, $CHPhEt·CH(CO_2Et)_2$, b. p. 187—188°/22 mm., prepared by the action of magnesium ethyl bromide on ethyl benzylidenemalonate, is a colourless liquid; the corresponding *acid*, m. p. 74°, crystallises with $1H_2O$.

Magnesium phenyl bromide reacts with phenyl formylethyl ketone to form a product which yields benzylidenepropiophenone. With magnesium ethyl bromide a substance was obtained consisting of impure phenyl α-methylbutenyl ketone, which was identified by means of its *dibromide*, m. p. 67°, and also by its conversion into phenyl β-phenyl-α-methylbutyl ketone by the action of magnesium phenyl bromide. *Phenyl β-phenyl-α-methylbutyl ketone*,

$$CHPhEt·CHMe·COPh,$$

m. p. 60·5°, prepared by the action of magnesium ethyl bromide on benzylidenepropiophenone, forms white, slender needles; its *oxime* has m. p. 119°.

Ethyl ethoxymethylenemalonate reacts with magnesium phenyl bromide with formation of a product which yields ethyl diphenylmethylmalonate; on treating this ester with alcoholic potassium hydroxide, *potassium ethyl diphenylmethylmalonate* is obtained. When ethyl ethoxymethylenemalonate is treated with magnesium ethyl bromide, *ethyl α-ethylpropylmalonate*, $CHEt_2·CH(CO_2Et)_2$, b. p. 138°/21 mm., is obtained as a colourless, mobile liquid.

β-Ethoxypropiophenone reacts with magnesium phenyl bromide with formation of *diphenylethoxyethylcarbinol*,

$$OEt·CH_2·CH_2·CPh_2·OH,$$

b. p. 207°/21 mm., m. p. 78°, which crystallises in white plates. This ketone also reacts with magnesium ethyl bromide with production of *phenylethylethoxyethylcarbinol*, $OEt·CH_2·CH_2·CPhEt·OH$, b. p. 151°/24 mm., as a colourless, mobile liquid.

Phenyl β-ethoxystyryl ketone can be obtained in fair yield by boiling phenyl dibromostyryl ketone with sodium ethoxide. This ketone reacts with magnesium ethyl bromide in presence of the usual quantity of ether to form a product, which, when decomposed with hydrochloric acid at 0°, yielded ethoxydiphenylethylallyl alcohol, together with ethoxyphenylethylpropiophenone and two solid *compounds*, $C_{34}H_{32}O_3$, one of which has m. p. 205° and forms white needles, whilst the other has m. p. 185° and forms yellow needles; the white substance slowly changes in solution into the yellow compound. *Ethoxydiphenylethylallyl alcohol*,

$$OEt·CPh{:}CH·CPhEt·OH,$$

m. p. 60·5°, crystallises in white, slender needles. *Ethoxyphenylethylpropiophenone*, $OEt·CPhEt·CH_2·COPh$, b. p. 96°/18 mm., is a colourless, mobile liquid; its *semicarbazide-semicarbazone* has m. p. 161°. In another experiment on the action of magnesium ethyl bromide on phenyl β-ethoxystyryl ketone, a much larger quantity of ether was used, and, on decomposing the product, the same three solid compounds were obtained, together with *γε-diphenyl-Δ^{βδ}-heptadiene*, $CPhEt{:}CH·CPh{:}CHMe$, b. p. 191—195°/20 mm., as a colourless liquid. When phenyl β-ethoxystyryl ketone is added to magnesium phenyl bromide in presence of a large quantity of ether, and the product is decomposed in the usual way, tetraphenylallyl alcohol is

obtained, but if the reaction is carried out in presence of only the usual quantity of ether, *ethoxytriphenylallyl alcohol*,

$$OEt\cdot CPh\colon CH\cdot CPh_2\cdot OH,$$

m. p. 120·5°, is produced, which crystallises in white, slender needles.

These experiments with phenyl β-ethoxystyryl ketone show that in the reaction between organic magnesium compounds and unsaturated compounds having an alkyloxy-group in the β-position, either αβ- or αδ addition takes place, and the alkyloxy-group of the resulting substance may or may not be replaced subsequently by a hydrocarbon residue. It is also shown that the influence of the β-ethoxy-group on the mode of addition is approximately the same as that of the phenyl group. E. G.

Action of Light on Unsaturated Ketones in Presence of Uranyl Salts. PAUL PRAETORIUS and FRANZ KORN (*Ber.*, 1910, **43**, 2744—2746).—Distyryl ketone, when exposed to the action of light in presence of uranyl chloride in acetic acid suspension, yields a colourless compound, $(C_{17}H_{14}O)_2$, m. p. 245° (decomp.), crystallising in needles. On oxidation with chromic acid, α-truxillic acid, benzoic acid, and carbon dioxide are formed. Accordingly, the formula

$$CHPh\colon CH\cdot CO\cdot CH<\begin{matrix}CHPh\\CHPh\end{matrix}>CH\cdot CO\cdot CH\colon CHPh$$

is assigned to the bimolecular compound.

A by-product is a substance soluble in acetic acid, which crystallises in colourless needles, m. p. 183°.

The red di-*p*-methoxydistyryl ketone uranyl chloride is stable towards light.

Dibenzylidene*cyclo*pentanone uranyl chloride is decomposed to a colourless compound, crystallising in pointed prisms, m. p. 248°, which gives an orange-yellow coloration with concentrated sulphuric acid.

E. F. A.

Existence of 2:2′-Dinitrobenzoin. THOR EKECRANTZ and ALFR. AHLQVIST (*Ber.*, 1910, **43**, 2606—2609. Compare Abstr., 1908, i, 347; Popovici, Abstr., 1907, i, 628).—A modification of Popovici's method (Abstr., 1908, i, 550) for the preparation of the so-called 2:2′-dinitrobenzoin is described, and the yield is increased to 0·4 gram from 25 grams of aldehyde. The product melts at 168—169° (corr.), not 161—162°, contains two atoms of hydrogen more than the benzoin, and is not oxidised to any appreciable extent by chromic acid mixture. J. J. S.

Colour and Affinity for Mordants of Anthraquinone Derivatives. II. GUSTAV HELLER (*Ber.*, 1910, **43**, 2890—2892. Compare Abstr., 1908, i, 995).—According to previous workers, the salts of anthraquinone-2:3-dicarboxylic acid, as well as those of the 1:3- and 1:4-acids, are reddish (compare Elbs and Eurich, Abstr., 1890, i, 511). Since this does not agree with the view put forward in the former paper, the author has prepared these substances, and finds that their alkaline solutions are colourless when pure. Nevertheless, they are fixed to a certain extent by some metallic hydroxides.

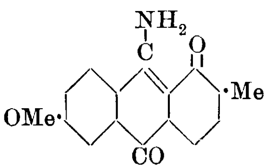
[With ERICH GRÜNTHAL.]—*o*-Xyloyl-*o*-benzoic acid, prepared by the Friedel and Crafts' reaction according to the method previously described (Abstr., 1908, i, 994), has m. p. 167° (F. Meyer, Abstr., 1882, 848, gave 161·5°).

2 : 3-Dimethylanthraquinone has m. p. 205—206° (Elbs and Eurich gave 183°; Limpricht, Abstr., 1900, i, 599, gave 200°).

1 : 4-Dimethylanthraquinone has m. p. 140—141° (Elbs and Eurich gave 118—119°). R. V. S.

Chrysophanic Acid. OTTO A. OESTERLE and U. JOHANN (*Arch. Pharm.*, 1910, **248**, 492—500).—The dimethyl ether, obtained together with a little monomethyl ether by treating chrysophanic acid with methyl sulphate, is partly demethylated by concentrated sulphuric acid on the water-bath or by aluminium chloride at 115°, yielding only one methyl ether, identical with the above. Consequently the hydroxyl groups in chrysophanic acid are not methylated with equal ease; the one which is easily methylated occupies probably a β-position, the other an α-position. Ethyl chloroacetate is a reagent which readily attacks hydroxyl groups in the α-position (D.R.-P. 158277); its action on chrysophanic acid, however, does not lead to definite results; the authors claim from them, however, that one hydroxyl group is probably in a β-position.

Chrysophanic acid methyl ether and aqueous ammonia, at 140°, yield a *substance*, $C_{16}H_{13}O_3N,\frac{1}{2}H_2O$, m. p. 237—239°, which crystallises in brownish-red needles, and has the composition of an amino-chrysophanic acid methyl ether; it is converted by nitrous acid into chrysophanic acid methyl ether, a reaction which is explained, in accordance with Scholl and Parthey's results (Abstr., 1906, i, 439), by ascribing to the substance



the annexed constitution, assuming that the hydroxyl groups in chrysophanic acid are in positions 1 and 6 and the methyl group in position 2. C. S.

So-called Methylchrysophanic Acid. OTTO A. OESTERLE and U. JOHANN (*Arch. Pharm.*, 1910, **248**, 476—491).—Chrysophanic acid, when prepared from rhubarb or chrysarobin, is accompanied by a substance containing methoxyl, which is stated by Hesse to be methylchrysophanic acid (Abstr., 1900, i, 41). Gilson claims that in the case of chrysophanic acid from rhubarb the accompanying substance is rheochrysidin (*Arch. internat. Pharm. Thér.*, 1905, **14**, 492). The authors show, however, that in chrysophanic acid from both sources the accompanying substance is the methyl ether of frangula-emodin. Chrysophanic acid, obtained by the oxidation of chrysarobin in alkaline solution, is methylated in the manner described previously (Abstr., 1905, i, 911), and the yellow substance, m. p. 224°, accompanying the dimethyl ether is separated therefrom by dilute alcohol; it has after repeated recrystallisation m. p. 226—227° and the composition of a trimethoxymethylanthraquinone. It can be demethylated by aluminium chloride at 115°, or, better, by concentrated sulphuric acid at 160°,

yielding a substance, m. p. 256—257°, identical with frangula-emodin (Abstr., 1908, i, 350), the identity being confirmed by a comparison of the *triacetates*, $C_{14}H_4O_2Me(OAc)_3$, yellow needles, m. p. 197—198°. Hence, the substance accompanying chrysophanic acid, obtained from chrysarobin, is a methyl ether of emodin. It can be isolated, although with considerable difficulty, by extracting the acetylated acid with alcohol at 50—55°; the acetate of emodin methyl ether thus obtained has m. p. 181—183°, but it still contains a little acetate of chrysophanic acid, because after hydrolysis, recrystallisation of the hydrolysed product, and re-acetylation, the m. p. is 190—191·5°. The hydrolysis of the acetate by aqueous potassium hydroxide yields an *emodin methyl ether*, $C_{14}H_4O_2Me(OH)_2{\cdot}OMe$, orange-red needles, m. p. 206—207°, identical with that obtained by the partial demethylation of frangula-emodin trimethyl ether by aluminium chloride at 115° for three-quarters of an hour. The ether dissolves in dilute alkali hydroxides with an intense red colour, and forms a *dipropionate*, m. p. 162—164°. It is shown to be identical with Gilson's rheochrysidin by its crystallographic properties, and with Hesse's physcion (lichen-chrysophanic acid) (Abstr., 1906, i, 280) by a comparison of the *dibenzoates*, m. p. 230°, and of the products of reduction by zinc and acetic acid. C. S.

Some Derivatives of Acenaphthenequinone. M. Zsuffa (*Ber.*, 1910, **43**, 2915—2922).—Naphthalic anhydride does not enter into the Friedel and Crafts' reaction with aromatic hydrocarbons, so that the carbonyl groups in the 1:8-position behave differently from those in the 1:2-position, as in phthalic anhydride. Acenaphthenequinone, $C_{10}H_6{<}\begin{matrix}CO\\|\\CO\end{matrix}$, however, readily undergoes this and other condensations. With aromatic hydrocarbons or with chlorobenzene, diaryl derivatives of the type $C_{10}H_6{<}\begin{matrix}CAr_2\\|\\CO\end{matrix}$ are produced, and these are even more readily obtained from dichloroacenaphthenone, $C_{10}H_6{<}\begin{matrix}CCl_2\\|\\CO\end{matrix}$. Acenaphthenequinone also condenses in a similar manner with dimethylaniline in the presence of zinc chloride or of concentrated hydrochloric acid, and with phenols (resorcinol) in presence of zinc chloride or tin chloride. From 9:9-diphenylacenaphthenone, diphenyl-α-naphthylmethane can be prepared with good yield, whilst from 9:9-tetramethyldiaminodiphenylacenaphthenone the corresponding hydrocarbon can also be prepared. The latter is readily oxidised to the naphthyl analogue of malachite-green.

9:9-Diphenylacenaphthenone (Beschke, Abstr., 1909, i, 918) can be obtained from acenaphthenequinone, or, better (yield almost quantitative), from dichloroacenaphthenone. In the latter case the action is vigorous, and should be moderated by the use of a solvent (carbon disulphide). When the substance is heated with alcoholic potassium hydroxide for four hours on the water-bath, 8-*diphenylmethyl*-1-*naphthoic acid*, $C_{24}H_{18}O_2$, crystallising in small, colourless laminæ, m. p. 227°, is obtained. On distillation in a vacuum with two and a-half times its weight of barium hydroxide, this yields *diphenyl-α-naphthylmethane*,

$C_{10}H_7\cdot CHPh_2$, which forms colourless needles, m. p. 150°. 8-Diphenylmethyl-1-naphthoic acid, when oxidised with chromic acid, gives *diphenylnaphthalide*, $C_{10}H_6<\begin{smallmatrix}CPh_2\\CO--\end{smallmatrix}>O$, which crystallises in colourless needles, m. p. 204°.

9 : 9-*Dichlorodiphenylacenaphthenone*, $C_{24}H_{14}OCl_2$ (from dichloroacenaphthenone and chlorobenzene), forms small, colourless needles, m. p. 151°. 8-*Dichlorodiphenylmethyl*-1-*naphthoic acid*, $C_{24}H_{16}O_2Cl_2$, crystallises in small, colourless laminæ, m. p. 224—225°.

9 : 9-*Tetramethyldiaminodiphenylacenaphthenone*, $C_{28}H_{26}ON_2$, is prepared by heating acenaphthenequinone with dimethylaniline and a small quantity of concentrated hydrochloric acid to 150° for three hours. It forms small, yellow laminæ or needles, m. p. 204—205°. Its solution in glacial acetic acid is coloured malachite-green by oxidising agents, but the coloration disappears on dilution with water. Prolonged boiling with alcoholic potassium hydroxide leaves the compound unaffected. The *hydrochloride*, $C_{28}H_{26}ON_2,2HCl$, prepared with hydrogen chloride in benzene solution, forms colourless needles, which with water regenerate the base. The *picrate*,

$$C_{28}H_{26}ON_2,2C_6H_3O_7N_3,$$

forms lemon-yellow crystals. The *dimethiodide*, $C_{28}H_{26}ON_2,2MeI$, has m. p. 224—225° (decomp.). When 9 : 9-tetramethyldiaminodiphenylacenaphthenone is boiled for four hours with amyl-alcoholic potassium hydroxide, 8-*tetramethyldiaminodiphenylmethyl*-1-*naphthoic acid*, $C_{28}H_{28}O_2N_2$, is obtained. It crystallises in pale yellow needles, m. p. 260—262°, and is soluble in acids and alkalis. The *barium* salt is sparingly soluble in water. Distillation of the acid with barium hydroxide yields *tetramethyldiaminodiphenyl-a-naphthylmethane*, $C_{10}H_7\cdot CH(C_6H_4\cdot NMe_2)_2$, which forms yellow needles, m. p. 161—162°, and on oxidation gives *naphthyl-malachite-green*.

Anhydrodiresorcinolacenaphthenone, $\begin{smallmatrix}C_{10}H_6\\|\\CO\end{smallmatrix}>C<\begin{smallmatrix}C_6H_3\cdot OH\\C_6H_3\cdot OH\end{smallmatrix}>O$, is prepared by heating acenaphthenequinone with resorcinol and zinc chloride for two hours at 180°. It is a pale brown, amorphous powder, which is soluble in alkali hydroxides, giving a yellowish-red coloration and a green fluorescence. R. V. S.

Derivatives of the Dextro-Antipode of Natural *l*-Menthol.

LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 714—718. Compare Skwortzoff, *ibid.*, 1910, **42**, 55).—The oil of Bucco leaves, freed from diosphenol by repeated treatment with 20% alkali hydroxide, was dried and fractionated. The fraction boiling at 190—225° was reduced with sodium and alcohol, the product distilled in steam, and the distillate then extracted with ether, dried, and redistilled. The fraction boiling at 200—220°, containing most of the menthol, was then converted into sodium menthylxanthate, which, by the action of iodine, was converted to the *disulphide*, thus:

$$C_{10}H_{19}O\cdot CS_2Na + 2I = S_2(CS\cdot O\cdot C_{10}H_{19})_2 + 2NaI,$$

m. p. 92—92·5°, $[\alpha]_C$ +183·4°, $[\alpha]_D$ +226·3°.

The latter with potassium cyanide gave the *anhydride*, $(C_{10}H_{19}O\cdot CS)_2S$, m. p. 147·5—148°, forming yellowish-green, hexagonal crystals,

In toluene solution at 20° it gave $[\alpha]_D$ + 46·42°, + 46·50°, $[\alpha]_E$ + 21·17°, the corresponding *l*-menthylxanthic anhydride giving $[\alpha]_D$ − 46·50°, $[\alpha]_E$ − 21·30°. The new compound must therefore be a derivative of *d*-menthol, and the two substances are optical antipodes. The disulphide of *l*-menthol has $[\alpha]_D$ − 182·8°, $[\alpha]_D$ − 225·1°. By saponification the *d*-menthylxanthic anhydride yields a menthol, m. p. 42°. Z. K.

Constitution of Fenchone. V. and VI. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 963—968, 968—973).—These two papers are in continuation of work published previously (this vol., i, 686), and record results given already in part (Abstr., 1909, i, 497, 595). Fuller experimental details and an outline of the principles underlying the syntheses effected are now given.

The following results are new. *apo*Fenchene hydrochloride (Abstr., 1908, i, 193), treated in succession with magnesium ethyl bromide and carbon dioxide, furnishes an acid having the same boiling point as dihydrofencholenic acid, but yielding an anhydride having b. p. 202°/20 mm., which is 3° lower than that of the expected anhydride (this vol., i, 573), and an amide, having m. p. 104°, as against 108° for dihydrofencholenamide, although it forms nacreous leaflets in all respects similar to those formed by the latter. T. A. H.

Action of Magnesium on a Mixture of Allyl Bromide and Pulegone (Synthesis of 1-Methyl-3-allyl-4-*iso*propylidene*cyclo*hexan-3-ol). G. G. VON FERSEN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 681—683).—1-*Methyl*-3-*allyl*-4-iso*propylidene*cyclo*hexan*-3-*ol*,

$$\begin{array}{l}\text{CHMe}\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_5)\cdot\text{OH} \\ \text{CH}_2\text{——CH}_2\cdot\text{C:CMe}_2\end{array},$$

obtained when magnesium is treated with a small quantity of allyl bromide and a mixture of pulegone and allyl bromide then added drop by drop, has b. p. 135—135·5°/27 mm., $D_4^{21·95}$ 0·9264, n_D 1·49039; it is a colourless liquid with a pleasant odour, which on oxidation with permanganate yields a complex mixture of acid and neutral products. Z. K.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. II. α-Pinene-*o*-hydroxylamineoxime. GUIDO CUSMANO (*Gazzetta*, 1910, 40, ii, 122—131. Compare this vol., i, 685).—From α-pinene bisnitrosochloride, the author has prepared α-pinene-*o*-hydroxylamineoxime similarly to the *d*-limonene-*o*-hydroxylamineoxime previously described (*loc. cit.*), but he has found that the compound reacts like the ordinary *m*-hydroxylamineoximes, so that the anomalous behaviour of the *d*-limonene derivative still requires explanation.

α-*Pinene*-o-*hydroxylamineoxime* forms lustrous needles, which decompose about 140°. It reduces Fehling's solution in the cold, and is soluble in alkalis, whilst with acids it yields monobasic salts. The *hydrochloride*, $C_{10}H_{18}O_2N_2$,HCl, which is formed in addition to the free base in the preparation of the substance, crystallises in tufts of silky needles, m. p. about 170°; when the solvent contains water, it

crystallises in hexagonal laminæ with $1H_2O$, and these sinter at about 100°, decomposing at 165°. The *sulphate*, $C_{10}H_{18}O_2N_2,H_2SO_4$, forms four-sided tablets. By the action of nitrous acid on either of these salts, the *iso*nitroamineoxime is formed (compare this vol., i, 574). The hydroxylamine group of the hydroxylamineoxime reacts with aldehydes. The *pentylidene* derivative,

$$OH\cdot N:C_{10}H_{15}\cdot N<\overset{CH\cdot C_4H_9}{\underset{O}{|}},$$

forms flat, quadrangular crystals, m. p. 150°. The *benzylidene* derivative, $OH\cdot N:C_{10}H_{15}\cdot N<\overset{CHPh}{\underset{O}{|}}$, crystallises in hexagonal laminæ, m. p. 167°. The p-*nitrobenzylidene* compound, $C_{17}H_{21}O_4N_3,C_2H_6O$, forms yellow crystals, m. p. 163—165°.

Pinene-*o*-hydroxylamineoxime is decomposed by very dilute oxalic acid, with formation of carvoxime and hydroxydihydrocarvoxime, so that instead of the elimination of the oxamic grouping, the destruction of the piceanic ring is effected. These two substances are formed in all the reactions in which the hydroxylamineoxime reacts in an acid medium, and hence they occur as by-products in its preparation. By the action of alkalis, the hydroxylamineoxime in time loses the oxamic group, hydroxylamine and nitrosopinene being formed.

o-*Nitroso*iso*nitrosopinene*, $C_{10}H_{15}<^{NO}_{N\cdot OH}$, may be obtained by oxidising α-pinene-*o*-hydroxylamineoxime, preferably by dissolving it in dilute sulphuric acid and adding the calculated quantity of potassium dichromate, the dilute solutions being kept cool with ice. It is a crystalline substance, which explodes at about 60°, and readily oxidises in the air, absorbing one atom of oxygen, with production of a yellow *substance*. When a solution of the hydroxylamineoxime hydrochloride is treated with iron alum, a *substance* is obtained containing 5·1% of iron; it is orange-yellow in colour, and decomposes at 110—120°.

R. V. S.

[Essential Oils.] Heinrich Haensel (*Berichte von H. Haensel*, April to September 1910, 6—53).—The flowers of *Gnaphalium avenarium*, used as an insectifuge, yielded 0·04% of dirty green, aromatic oil, which solidified at 4° and had D^{30} 0·921. After treatment with animal charcoal, it was bluish-green in colour, solidified at 7°, had acid number 14·45, ester number 9, and was incompletely soluble in 95% alcohol. The insoluble matter consisted of stearopten, m. p. 48—50°, containing a bluish-green colouring matter. The soluble portion of the oil contained (1) an *acid*, m. p. 34—36°, with an odour recalling that of hexoic acid, (2) *p*-cresol, and (3) an alcohol having a fruity odour.

Syrian peppermint oil (compare this vol., i, 401) gave a terpeneless fraction having the following constants: acid number 1·87, ester number 22·4, acetyl ester number 180 (one hour), corresponding with 6·24% ester menthol and 51·73% free menthol. The crude oil yielded 5% of terpene, having D^{18} 0·8880.

Datura Stramonium leaves yielded 0·045% of a volatile oil of dark brown colour and tobacco-like odour. It had D^{30} 0·9440, solidified at 20°, and after treatment with animal charcoal showed acid number

52·4, and ester number 9·57. The saponified oil contained a minute quantity of an alcohol having a strong odour of tobacco. The aqueous distillate was alkaline and of blue colour, but became colourless on addition of acid, regaining the blue colour on addition of alkali.

Dalmatian yellow sunflowers (Sonnengoldblumen) furnished 0·235% of oil, $D^{18.5}$ 0·9100, $\alpha - 5°10'$, of greenish-yellow colour and pleasant, sweet aroma. It had acid number 8·9 and ester number 87·66, corresponding with 24·12% of alcohol, $C_{16}H_{18}O$. T. A. H.

Spearmint Oil. F. ELZE (*Chem. Zeit.*, 1910, **34**, 1175).—The carvone-free residue of spearmint oil has an intense spearmint odour, and on distillation under reduced pressure gives the following fractions: b. p. 40—45°/4 mm., 15%, containing 2·8% esters; b. p. 45—75°/4 mm., 15%; b. p. 75—80°/4 mm., 24%, containing 19% esters; b. p. 80—85°/4 mm., 7·5%; and 85—100°/4 mm., 35·0%, containing 31% esters. From the first of these fractions phellandrene was isolated. The last fraction, freed from aldehydes and phenols, furnished on hydrolysis acetic and valeric acids and dihydrocuminyl alcohol. Dihydrocuminyl acetate has the characteristic odour of spearmint oil. T. A. H.

Cold Vulcanisation of Caoutchouc. B. B. BYSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 638—647).—A criticism of Weber's theory of the vulcanisation of caoutchouc with sulphur chloride, S_2Cl_2. The chemical explanation of the process is not satisfactory. Regarding caoutchouc as a heterogeneous disperse system consisting of two liquid phases, it will probably have the general properties of a colloid, such, for instance, as the property of adsorption. The change in caoutchouc on vulcanisation with sulphur chloride is due to the adsorption of the latter, the process of vulcanisation is thus physical not chemical. The connexion between the amount of sulphur contained in the caoutchouc after vulcanisation and the concentration of the benzene solutions of sulphur chloride employed has been studied, and the resulting curve, which is hyperbolic, is drawn. Z. K.

Chlorophyll Group. VIII. Formation of Phyllotaonin from Chlorophyllan. HENRY K. MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1910, **28**, 48—52. Compare this vol., i, 692).—When chlorophyllan (15 grams), obtained from stinging nettles, is left for twenty-four hours with 200 c.c. of methyl-alcoholic potassium hydroxide solution, hydrolysis takes place. The mass is poured into 2 litres of water, and the phytol removed by extraction with ether; acetic acid is added, and the ether extraction repeated. The ethereal solution is fractionated by extracting with gradually increasing amounts of hydrochloric acid, namely, from 1 to 20%. The product, soluble in 1% hydrochloric acid, contains chlorophyllanic acid, and the solution in 18% hydrochloric acid gives all the characteristic absorption bands of *allo*phyllotaonin (Kózniewski and Marchlewski, Abstr., 1907, i, 867), and when treated with alkalis gives the absorption bands of phyllotaonin. J. J. S.

Commercial Azolitmin. PAUL SCHEITZ (*Zeit. anal. Chem.*, 1910, **49**, 735—736. Compare following abstract).—Azolitmin occurs in commerce in the form of bluish-black scales, contains very little

mineral matter, dissolves in water with a red coloration, but becomes insoluble in water after heating at 100° during three to four hours. It dissolves in ammonia or alkali solutions, forming blue liquids, but is not re-precipitated therefrom by acids, the solutions merely changing colour to red. The substance appears to be an ammonium salt, since it evolves about 8·5% of ammonia on treatment with alkalis.

By dissolving commercial azolitmin in ammonia solution, recovering the colouring matter by adding excess of hydrochloric acid and warming, and then purifying the precipitated product by boiling with alcohol, about 22% of a nitrogenous substance closely resembling the azolitmin of litmus is obtained. This is greenish-black in colour, and almost insoluble in water, alcohol, or acetone; it absorbs ammonia gas, forming a bluish-black product, which dissolves in water, forming a red solution from which the purified azolitmin is regenerated on addition of excess of acid or salts of heavy metals. This ammonium compound is a useful indicator. Similar products are obtained with methylamine and dimethylamine. T. A. H.

The Portion of Litmus Soluble in Alcohol. PAUL SCHEITZ (*Zeit. anal. Chem.*, 1910, **49**, 736—739. Compare preceding abstract).—The isolation of a blue colouring matter distinct from azolitmin and soluble in alcohol is described. When crude litmus is treated with dilute hydrochloric acid until no more carbon dioxide is evolved, the red solution formed slowly deposits, when warmed at 100°, a dark brown precipitate, which, when boiled with water, separates into (*a*) a finely-divided reddish powder, containing some azolitmin, but consisting chiefly of products soluble in alcohol, and (*b*) a grey-steel product, mainly composed of azolitmin, but containing a little alcohol-soluble matter.

When boiled with a mixture of alcohol (2 parts) and water (1 part), preparations *a* and *b* furnish (1) azolitmin, insoluble in aqueous alcohol, and (2) a mixture of Kane's erythrolein and erythrolitmin with a third substance, which is bright brown in colour, all of these being soluble in hot aqueous alcohol. Of these three substances the first two can be eliminated by extraction with hot acetone, leaving the third in an impure form, from which a purer form can be prepared by dissolving it in hot aqueous alcohol, filtering, and cooling, when it is deposited as bright brown powder, equivalent in weight to 1·5% of the purified litmus. This is soluble in formic acid, pyridine, or ammonia, forming a bluish-violet solution with the last-mentioned solvent. It absorbs ammonia gas, becoming hot, and forming a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin (compare preceding abstract). Similar substances are formed by absorption of methylamine and dimethylamine. T. A. H.

Phycoerythrin and Phycocyanin from Ceramium rubrum (Huds.). HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1910, **69**, 169—239. Compare Hanson, Proc., 1909, **25**, 117; Molisch, Abstr., 1895, i, 556; 1906, ii, 118; Gaidukov, *ibid.*, 1904, i, 439).—Details are given for the preparation of solutions of pure phycoerythrin and phycocyanin from *Ceramium rubrum.* The isolation is based on the

fact that both colouring matters can be obtained in a crystalline form by the addition of the requisite amount of ammonium sulphate to their solutions; the phycocyanin is deposited when 18 grams of sulphate, and the phycoerythrin when 25 grams of sulphate, have been added to 100 c.c. of the solution. Magnesium sulphate may also be used, but larger quantities are necessary. Phycocyanin can be precipitated in an amorphous state by completely saturating its solution with sodium chloride, but phycoerythrin is not precipitated under these conditions.

The phycoerythrin solution has a carmin-red colour, and when dilute a tinge of violet; concentrated solutions have an orange colour, and all solutions give a characteristic orange-yellow fluorescence. It gives all the characteristic reactions of a protein, including the biuret reaction (compare Hanson). The colouring matter dissolves in water containing a small amount of alkali or of neutral salts, but is deposited in a crystalline form when all salts are removed by dialysis. It is insoluble in ordinary organic solvents, but dissolves in dilute acetic acid and also in extremely dilute hydrochloric acid, yielding solutions which do not fluoresce.

The conclusion is drawn that the acid decomposes the phycoerythrin into protein and colouring matter, and that the precipitate obtained on adding a small amount of sodium carbonate to the acid solution is the colour-constituent. The addition of a trace of acid to the ordinary solution precipitates the phycoerythrin.

The small amounts of salts which are necessary to keep the colouring matter in solution are sufficient to cause complete precipitation when the solution is heated at 90°. The addition of traces of acid reduce the temperature of coagulation, and the amount of acetic acid necessary to give the ordinary protein reaction produces coagulation at 53—55°. The addition of a trace of alkali prevents coagulation.

The action of pepsin and trypsin is represented as first causing a decomposition of the phycoerythrin into protein and colour-constituents, and then the decomposition of the protein. After the digestion with pepsin, the colour-constituent can be removed by shaking with amyl alcohol. The results of analyses of phycoerythrin gave: $C = 50{\cdot}82$, $H = 7{\cdot}01$, $N = 15{\cdot}37$, $S = 1{\cdot}60$, and $O = 25{\cdot}20\%$.

The absorption spectrum of pure phycoerythrin contains three characteristic bands, two between *D* and *E*, and one between *E* and *F*. These bands have their maxima at $\lambda = 569$—565, 541—537, and 498—492 $\mu\mu$. On dilution the second band disappears before the third.

Phycocyanin crystallises in rhombic plates, quite different from the crystals described by Molisch. It gives the protein reactions; its solubility in water, saline solutions, and dilute alkalis is similar to that to phycoerythrin, as is also its behaviour towards acids, pepsin, and trypsin.

A solution of phycocyanin containing the smallest possible amount of salt is completely coagulated when heated at 82°, and the addition of a little acetic acid reduces this to 46—48°.

The solutions of phycocyanin exhibit two absorption bands, one between *C* and *D* and the other between *D* and *E*, the maxima being at λ 618—613 and 553—549 $\mu\mu$. J. J. S.

Sulphur Dyes. II. HERMANN WICHELHAUS (*Ber.*, 1910, 43, 2922—2926. Compare Abstr., 1907, i, 232; Erdmann and Schäfer, this vol., i, 718).—The distillate from 20 kilograms of cellulose (cotton) consisted of 5·7 litres of an aqueous liquid and 1 litre of an oily mass. From both of these only one phenol could be isolated, namely, phenol itself. The author has put forward the view that a sulphur dye could be formed from phenol, thus explaining the origin of sulphur dyes from cellulose. As an intermediate product, phenoquinone claims attention. Molecular-weight determinations in the case of the analogous toluquinone and thiotoluquinone confirm the original statement (*Ber.*, 1872, 5, 248) that phenoquinone has the formula $C_{18}H_{14}O_4$. When it is boiled with alkali sulphides and sulphur, or, better, heated with those substances under pressure at 200—220°, a sulphur dye is formed, which, after purification, contains C 75%, H 5%, S 12%. It is a dark brown powder, insoluble in alkaline carbonates, ammonia, and acids, but soluble in alkali sulphides. The last-named solution dyes cotton dark brown.

Phenoquinone also yields a dye free from sulphur when it is kept for ten days at the ordinary temperature in contact with sodium acetate and water. The crude product is purified by solution in sodium hydroxide, re-precipitation with acid, removal of phenol by means of steam, and final precipitation as iron salt, which is decomposed by hot hydrochloric acid. So obtained, the acid has m. p. 110°. When dissolved in sodium carbonate, it dyes cotton brown.

Fluorescein yields sulphur dyes when heated with sulphur or sulphur and sodium sulphide, but it is not possible to obtain them in a pure state. Dithiofluorescein chloride,

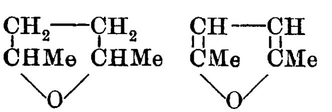
$$CS<\begin{matrix}C_6H_4\\ -S-\end{matrix}>C<\begin{matrix}C_6H_3Cl\\ C_6H_3Cl\end{matrix}>O,$$

which is not a dye, condenses in presence of sulphuric acid or anhydride to form sulphur derivatives which are dyes. R. V. S.

Velocity of the Transformation of Oxonium Bases, Colour Bases, and Cyanides into Carbinol Bases and Leucocyanides. WOLF. J. MÜLLER (*Ber.*, 1910, 43, 2609—2613. Compare this vol., i, 407; Gerlinger, Abstr., 1904, i, 1040).—The velocity constants of various reactions studied by Hantzsch and his pupils (Abstr., 1900, i, 113, 256) have been recalculated from Hantzsch's data, and it is shown that, using the equation for a bimolecular reaction, quite concordant values for *K* are obtained.

Hantzsch's statement to the contrary is due to mistakes in calculation. J. J. S.

Stereochemistry of 1 : 4-Dimethyltetrahydrofuran and 1 : 4-Dimethylfuran. ANGEL DEL CAMPO Y CERDÁN (*Anal. Fis. Quim.*, 1910, 8, 227—244).—A geometrical study of the causes of the difference of stability of the two compounds (annexed formulæ) from the point of view of the "tension" theory. It is shown that the mass of the groups in the first compound causes a greater strain or deforma-



tion from the simple regular tetrahedral form, representing a carbon atom combined with four hydrogen atoms, than those of the second; the latter is therefore the more stable substance, as is actually the case.

W. A. D.

ω-Hydroxy-s-methylfurfuraldehyde. HENRY J. H. FENTON (*Ber.*, 1910, **43**, 2795—2796. Compare Fenton and Gostling, Trans., 1899, **75**, 430; Fenton and Robinson, *ibid.*, 1909, **95**, 1338; Alberda van Ekenstein and Blanksma; Erdmann, this vol., i, 762).—Attention is drawn to the fact that the hydroxyfurfuraldehydes prepared from the ω-bromomethylfurfuraldehyde and from inulin by the action of oxalic acid are identical. They yield the same phenylhydrazone and the same oxidation product, and both are to be regarded as ω-hydroxy-s-methylfurfuraldehyde. J. J. S.

Triphenylmethyl. XIX. Quinocarbonium Salts. MOSES GOMBERG and LEE H. CONE (*Annalen*, 1910, **376**, 183—238. Compare Abstr., 1907, i, 504; 1909, i, 144; this vol., i, 55).—Not merely salts of triphenylmethane and xanthenol, but also those derived from diphenoxanthhydrol, dinaphthaxanthhydrol, thioxanthenol, and 4 bromothioxanthenol exist in colourless benzenoid and yellow quinonoid forms. The acridol salts are also regarded as quinocarbonium salts. Diphenoxanthhydrol exists in the solid form as the colourless benzenoid carbinyl chloride, and appears to be incapable of yielding a stable coloured chloride hydrochloride; it can, however, be readily transformed by means of sulphur dioxide, sulphuric acid, or metallic halides. Dinaphthaxanthhydrol, on the other hand, yields a perfectly stable and intensely coloured chloride dichloride in addition to the colourless carbinol chloride.

Xanthhydryl chloride, $O<\substack{C_6H_4\\C_6H_4}>CHCl$ (compare Werner, Abstr., 1902, i, 50), can be prepared by the action of hydrogen chloride on xanthhydrol in absolute ethereal solution. It is extremely sensitive to traces of moisture, but can be obtained in colourless needles, m. p. 73—75° after sintering at 71°. When further heated, hydrogen chloride is evolved, and at 170—175° the evolution is rapid. Hydrogen chloride is also evolved when the salt is heated with xylene or nitrobenzene, but whether dixanthylene is formed or not has not been determined. It does not yield a stable quinonoid hydrochloride, but the following double salts have been prepared: *zincichloride*, $C_{13}H_9OCl,ZnCl_2$, yellow, granular precipitate; ferrichloride,

$$C_{13}H_9OCl,FeCl_3,$$

m. p. 193° (compare Werner); *periodide*, $C_{13}H_9OCl,I_4$, prepared from benzene solutions, dark blue crystals, m. p. 90°.

Xanthhydryl bromide, $O:(C_6H_4)_2:CHBr$, is much more stable than the chloride, and crystallises from light petroleum solutions in long, colourless needles, m. p. 88—90°, which turn yellow when kept. The pure quinocarbonium salt has not been obtained, but the following double salts are described: *zincibromide*,

$$C_{13}H_9OBr,ZnBr_2,$$

slender, orange-yellow crystals; *periodide*, dark blue crystals with four or six atoms of iodine.

Xanthhydryl perchlorate, $C_{13}H_9O\cdot ClO_4$, forms dark red crystals, m. p. 208—209°.

Dinaphthaxanthen is best prepared by heating pure *p*-dihydroxynaphthylmethane (Manasse, Abstr., 1894, i, 577) with glacial acetic acid in a current of hydrogen chloride. Dinaphthaxanthhydrol can be prepared by Fosse's methods (Abstr., 1902, i, 171).

Dinaphthaquinoxanthhydryl chloride hydrochloride,

$$C_{10}H_6<\begin{matrix}CH:C\cdot C_6H_4\\ \quad\;| \\ O-C:CH\end{matrix}>CHCl,HCl,$$

prepared by the action of acetyl chloride and hydrogen chloride on a benzene solution of the hydrol or on the anhydride in chloroform solution, crystallises in dark red needles, m. p. 228—229° (decomp.), and is extremely stable. When a current of air is passed through its toluene solution at 100°, hydrogen chloride is evolved, and *dinaphthaxanthhydryl chloride*, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CHCl$, is precipitated on the addition of light petroleum to the concentrated solution as slender, colourless needles, m. p. 205—206°, which are comparatively stable. The *zincichloride*, $C_{21}H_{13}OCl,ZnCl_2$, forms a stable, orange-red, crystalline mass, and the *periodide*, $C_{21}H_{13}OCl,I_2$, is precipitated when iodine is added to a benzene solution of the chloride. *Dinaphthaquinoxanthhydryl bromide hydrobromide*, $C_{21}H_{13}OBr,HBr$, forms a red, crystalline mass, and is even more stable than the hydrochloride. The *perchlorate*, $C_{21}H_{13}O\cdot ClO_4$, forms red crystals with a golden reflex, is not molten at 260°, and is only slowly decomposed by water. Dinaphthaxanthen-reacts with a carbon disulphide solution of bromine, yielding a red *dinaphthaxanthhydryl bromide perbromide* according to the equation: $O:(C_{10}H_6)_2:CH_2 + 2Br_2 = O:(C_{10}H_6)_2:CHBr\cdot Br_2 + HBr$, even when less than the theoretical amount of bromine is used. Chlorine reacts with a carbon tetrachloride solution of the xanthen, yielding an insoluble chloride perchloride.

Phenylthioxanthenol, prepared by a modification of Bünzly and Decker's method (Abstr., 1904, i, 912), reacts with a mixture of acetyl and hydrogen chlorides in chloroform solution, yielding *phenylquinothioxanthenyl chloride hydrochloride*, $\begin{matrix}HCl,CHCl\cdot CH:C---S\\ \;\;|\qquad\qquad\quad | \\ CH=CH\cdot C:CPh\end{matrix}>C_6H_4$, in the form of dark red crystals, the colour of which is much deeper than that of the corresponding oxygen compound. When dry air is led through a benzene solution of the red compound, hydrogen chloride is evolved and *phenylthioxanthenyl chloride*, $S<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>SPhCl$, is formed. This crystallises from light petroleum in colourless prisms, m. p. 114—115°, after sintering at 110°, and turns red on exposure to the air. The chloride reacts with "molecular" silver in the presence of dry benzene, yielding a brownish-red, unsaturated compound, which is stable in the absence of air, but combines readily with oxygen, yielding the *peroxide*, $S:(C_6H_4)_2:CPh\cdot O\cdot O\cdot CPh:(C_6H_4)_2:S$,

which crystallises in colourless, hexagonal prisms, m. p. 187—188°, after sintering at 175—180°.

The *2-phenylthiol-4-bromobenzoic acid*, $C_{13}H_9O_2SBr$, prepared by Goldberg's method (Abstr., 1905, i, 59), crystallises from glacial acetic acid, has m. p. 230—231°, and when warmed with concentrated sulphuric acid and then diluted yields *4-bromothioxanthone*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CO,$$

as slender, yellow needles, m. p. 165°, which reacts with phenyl magnesium bromide, yielding *4-bromo-9-phenylthioxanthenol*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CPh\cdot OH,$$

as an oil, from which a few crystals, m. p. 75—80°, can be obtained. *4-Bromo-9-phenylquinothioxanthenyl bromide hydrobromide*,

$$C_{19}H_{12}SBr_2,HBr,$$

forms dark red needles, which are immediately decomposed by moisture. *4-Bromo-9-phenylthioxanthenyl bromide*,

$$S<\begin{matrix}C_6H_4\\C_6H_3Br\end{matrix}>CPhBr,$$

is usually slightly coloured, has m. p. 159°, after sintering at 150°, and after treatment with silver it does not yield a peroxide. In this respect it resembles the monohalogenated triphenylmethyl halides, as also in the readiness with which the two atoms of bromine are replaced by chlorine when the bromide is shaken with benzene and silver chloride.

4-Chloro-9-phenylquinothioxanthenyl chloride hydrochloride,

$$C_{19}H_{12}SCl_2,HCl,$$

obtained by shaking the corresponding tribromo-derivative with benzene and silver chloride, or by saturating the benzene solution with hydrogen chloride, is somewhat paler in colour than the bromide, and gives up hydrogen chloride when dry air is passed through its benzene solution at the ordinary temperature. The product, *4-chloro-9-phenylthioxanthenyl chloride*, $C_{19}H_{12}SCl_2$, is readily soluble in all solvents, and has not been obtained pure. *9-Phenylthioxanthenyl perchlorate*, $C_{19}H_{13}S\cdot ClO_4$, crystallises in slender, dark red plates, m. p. 195—210°, after sintering at 150°, and *thioxanthone perchlorate*, $C_{13}H_9OS\cdot ClO_4$, in transparent, brown prisms.

A number of compounds of dimethylpyrone, benzo-γ-pyrone, xanthone, aldehydes, ketones, and phenols with acids have been prepared. Many of them have been described previously (compare Collie and Tickle, Trans., 1899, **75**, 710; Feist, Abstr., 1892, 811; Baeyer and Villiger, Abstr., 1901, i, 658; Vorländer, Abstr., 1903, i, 495; Werner, Abstr., 1902, i, 686; Ruhemann, Trans., 1900, **77**, 985, 1123), but the following are new. Dimethylpyrone derivatives: $(C_7H_8O_2)_2ZnCl_2$, colourless crystals, m. p. 200°; *zincichloride*, $(C_7H_8O_2,HCl)_2ZnCl_2$, colourless, hygroscopic crystals; $C_7H_8O_2,HgCl_2$, colourless crystals, m. p. 149°; *mercurichloride*, $C_7H_8O_2,HCl,HgCl_2$; *ferrichloride*, $3C_7H_8O_2,2FeCl_3$, lemon-yellow crystals, m. p. 173—174°; *hydrobromide*, $C_7H_8O_2,HBr$, m. p. 194—196°, after sintering at 188°; $2C_7H_8O_2,ZnBr_2$, colourless crystals, m. p. 204—205°. Derivatives of

benzo-γ-pyrone: *hydrochloride*, $C_9H_6O_2,HCl$, m. p. 101—102° (decomp.); $C_9H_6O_2,ZnCl_2$, colourless crystals, m. p. 250—251°, after sintering at 205°; *zincichloride*, $(C_9H_6O_2,HCl)_3ZnCl_2$; $C_9H_6O_2,HgCl_2$, colourless crystals; *hydrobromide*, $C_9H_6O_2,HBr$, m. p. 175°, after sintering at 169°; *hydrobromide periodide*, dark blue crystals.

The hydrochloride and hydrobromide of dimethylpyrone are decomposed when heated with benzene and a current of dry air drawn through the solution, and the salts of benzo-γ-pyrone are even less stable. Dimethylpyrone does not appear to react with phenyl magnesium bromide.

Although Perkin (Trans., 1896, **69**, 1439) states that xanthone does not combine with acids, the following compounds have been prepared: *xanthone hydrochloride periodide*, prepared by passing hydrogen chloride into a carbon disulphide solution of xanthone and iodine; *xanthone hydrobromide*, $C_{13}H_9O_2Br$, is unstable and forms pale yellow crystals; the *perbromide*, $C_{13}H_8O_2,HBr,Br_2$, forms orange-coloured crystals and gives up bromine readily; *β-phenonaphthaxanthone hydrobromide*, $C_{17}H_{10}O_2,HBr$, forms yellow needles; *5-methoxyxanthone hydrobromide*, $C_{14}H_{10}O_3,HBr$, pale yellow crystals, and *xanthone stannichloride*, $(C_{13}H_8O_2)_2SnCl_4$, pale yellow crystals, m. p. 245°.

These compounds are compared with the additive compounds formed by the union of carbonyl derivatives with acids and salts. In the latter group of additive compounds the acid, for example, hydrogen chloride, is, almost undoubtedly, added on to the carbonyl group, and it is suggested that probably the same type of reaction takes place with dimethylpyrone, xanthone, etc. The products are probably not salts, and their decomposition into oxygen compound plus acid is probably not a process of hydrolysis, but of dissociation (addenda-dissociation of Vorländer).

Fluorenone hydrobromide periodide, $C_{13}H_8O,HBr,I_3$, forms coloured crystals; *phenanthraquinone hydrobromide*, $C_{14}H_8O_2,HBr$, is unstable, and anthraquinone does not appear to yield a hydrobromide. Anisaldehyde hydrobromide (compare Vorländer) is stable, and can be prepared at the ordinary temperature. *p*-Hydroxybenzaldehyde, resorcylaldehyde, piperonal, vanillin, and β-naphtholaldehyde all yield comparative stable, yellow *hydrobromides.*

Phenols which can react in the tautomeric ketonic forms can also form hydrobromides, for example, orcinol, phloroglucinol, and quinol, whereas resorcinol, pyrogallol, guaiacol, and the methyl ethers of resorcinol, quinol, and pyrogallol do not combine with hydrogen bromide.

The application of the quinocarbonium theory to the cases of pararosaniline, phenylated rosanilines, amino-azines, aurin, phenolphthalein, fluorescein, and fluorone is discussed. The theory accounts for the fact that phenolphthalein is incapable of yielding a coloured hydrobromide, that fluorescein yields a mono-hydrobromide (Hewitt and Tervet, Trans., 1902, **81**, 663), and dimethylfluoran a *dihydrobromide*, $C_{22}H_{16}O_3,2HBr$, slender, orange-yellow crystals. J. J. S.

Brominated and Iodinated Products of Curare Alkaloids JÓZEF BURACZEWSKI and Z. ZBIJEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 352—354).—The two alkaloids, curine and tubocurarine, in commer-

cial tubocurare from the bamboo have been examined with regard to their behaviour towards bromine and iodine. Curine, in ethereal solution, gives with bromine a straw-yellow precipitate, probably of a dibromo-derivative, but does not yield a precipitate with iodine. An alcoholic solution, however, by treatment with iodine in carbon disulphide gives a brownish-red precipitate, which dissolves very easily in alkalis or in aqueous ammonia, being re-precipitated by acids in the form of an almost black substance containing 49·65% of iodine. Curine, therefore, resembles strychnine in its behaviour towards bromine, but not towards iodine. An alcoholic solution of tubocurarine and iodine in carbon disulphide give a similar precipitate of like properties. The formation of these iodinated products is of use in the examination of crude tubocurare, because the colour reactions of curine and tubocurarine are applicable only to the isolated alkaloids, not to crude tubocurare. C. S.

Action of Chlorine on Strychnine, Brucine, Cinchonine, Quinine, and Other Alkaloids. JÓZEF BURACZEWSKI and Z. ZBIJEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 355—362).—On account of the oxidising action of chlorine, chlorinated derivatives of the alkaloids are more difficult to prepare than brominated or iodinated derivatives. By passing a slow current of dry chlorine over the well-cooled and shaken dry alkaloids, the authors find that chlorinated products are obtained containing usually more halogen than is the case in the usual methods of chlorination; heat is developed and frequently hydrogen chloride given off, although sometimes only after some time. By this process, strychnine absorbs five atoms of chlorine, brucine three, cinchonine four, cinchonidine three, quinine six, quinidine six, thebaine four, and morphine one. In these chlorinated alkaloids at least a part of the halogen is bound in the same way as the halogen in the brominated or iodinated derivatives, because all of the products except the chlorinated morphine yield with warm water an insoluble precipitate and a soluble salt of a chlorinated base. C. S

Action of Acetone on Di-iodostrychnine and on the Brominated Products of Strychnine and of Some Other Alkaloids. JÓZEF BURACZEWSKI and MIECESLAS DZIURZYŃSKI (*Bull. Acad. Sci. Cracow*, 1910, 363—366).—Complicated reactions take place during the prolonged boiling necessary for the solution of di-iodostrychnine (Abstr., 1908, i, 1007) in acetone. Two colourless, non-poisonous, crystalline products are obtained, which do not exhibit the properties of strychnine or of its salts. Strychnine hydriodide and periodide, $C_{21}H_{22}O_2N_2I_2,HI$, are also produced, together with iodo-acetone. Dibromostrychnine and tetrabromostrychnine (and also pentabromoquinine) likewise cause the formation of bromoacetone when they are boiled with acetone. The formation of these halogenated acetones is regarded as evidence that the method of union of the two iodine atoms in di-iodostrychnine is the same as that of two bromine atoms in dibromo- or in tetrabromo-strychnine. C. S.

Oxidation Products of Brominated Strychnines. I. JÓZEF BURACZEWSKI and T. NOWOSIELSKI (*Bull. Acad. Sci. Cracow*, 1910, 154—162).—On account of the scarcity of characteristic oxidation products of strychnine and of their importance for the determination of its constitution, the authors have commenced a more thorough examination of the precipitates obtained by Buraczewski and Dziurzyński (Abstr., 1909, i, 672). These authors found that by warming dibromostrychnine with water a precipitate is formed; the bromostrychnine obtained from the filtrate yielded by bromination a mixture of tri- and tetra-bromostrychnines, which likewise yielded a precipitate when warmed with water. The basic substance obtained from the aqueous filtrate in the latter case has been brominated, yielding a product which again gives a precipitate when warmed with water. The first-mentioned precipitate dissolves almost completely in alcohol, but the others are separated by this solvent into a soluble and an insoluble portion. The insoluble portions behave alike towards alkalis, acids, and solvents, and are recrystallised, after being mixed, from hot acetic acid by the addition of water, yielding a *substance*, $C_{21}H_{20}O_3N_2Br_3$, which is dextrorotatory, non-poisonous, has no bitter taste, and is provisionally called *tribromostrychnine oxide*. The portions soluble in alcohol are combined and purified by precipitating the alcoholic solution with water containing hydrochloric acid; the product is amorphous (it has since been obtained crystalline in very small quantity), optically inactive, non-poisonous, and has a composition approximating to the formula $C_{21}H_{22}O_4N_2Br_3$. The aqueous filtrate, from which the last-mentioned precipitate has been separated, contains a substance which has pronounced basic properties, is lævorotatory, and is non-poisonous, but has an intensely bitter taste. C. S.

Alkaloids in the Roots of Sanguinaria canadensis TAD. KÓZNIEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 235—246).—Sanguinarine, isolated by Dana in 1828 from the roots of *Sanguinaria canadensis*, and proved by Schiel in 1842 to be identical with chelerithrine obtained by Probst from *Chelidonium majus*, has been shown to be a mixture of three alkaloids by Schmidt and his collaborators, who found that the roots of *Sanguinaria* contain five alkaloids, namely, sanguinarine (red salts), chelerithrine (yellow salts), protopine, and β- and γ-homochelidonine (colourless salts). The last two are easily separated from the first three by their solubility in aqueous ammonia, but the separation of sanguinarine, chelerithrine, and protopine presents very great difficulties. The author describes a comparatively simple method which depends on the formation of sparingly soluble salts. The alcoholic extract of the powdered roots is evaporated, and the residue is treated with 5% and with 10% acetic acid. Three-quarters of the mass remains undissolved (*P*), and is worked for sanguinarine as described below. The acetic acid solutions are cooled and treated with 40% sulphuric acid, whereby a crystalline precipitate is formed, which is collected after forty-eight hours and yields pure chelerithrine after further purification. The filtrate is cooled in a freezing mixture, and just basified with ammonia. The resulting precipitate is extracted with hot dilute acetic acid, and the solution is

treated with an excess of 40% sulphuric acid. The yellow, crystalline precipitate obtained yields a further quantity of chelerithrine, whilst the filtrate by treatment with ammonia gives a violet precipitate. This is dissolved in 10% acetic acid, and the solution treated with an excess of sulphuric acid. A third precipitate is thus obtained containing a considerable quantity of chelerithrine and sanguinarine; the precipitate obtained by adding ammonia to the filtrate is dissolved in 10% sulphuric acid, and the solution is treated with more sulphuric acid, whereby a fourth crystalline precipitate containing chelerithrine and sanguinarine is obtained, the filtrate being worked for protopine, which is finally isolated in the form of its hydrochloride.

The residue (*P*) is ground with kieselguhr and heated for three hours with 20% sulphuric acid. The red solution deposits a scarlet precipitate on cooling, from which pure sanguinarine is obtained by further purification. The fact that the residue requires prolonged heating with sulphuric acid for solution is taken as evidence that sanguinarine is present in the roots in the form of a stable compound which yields the alkaloid by hydrolysis.

From his analyses the author concludes that sanguinarine separates from solutions containing alcohol in crystals containing Et·OH; the m. p. of such crystals is 212°. Sanguinarine forms a *periodide*, $C_{20}H_{15}O_4NI_2,HI$, m. p. 205°, and chelerithrine, a *periodide*, $C_{21}H_{17}O_4NI_2,HI$, m. p. 225°, crystallising in ruby-red needles. C. S.

Reactions of 2 : 4 : 6-Trihydroxypiperidine Trisulphite. JULIUS SCHENKEL (*Ber.*, 1910, **43**, 2597—2601).—The additive compound of pyridine and sodium hydrogen sulphite, which is regarded as the trisulphite ester derived from 2 : 4 : 6-trihydroxypiperidine (compare Bucherer and Schenkel, Abstr., 1908, i, 452), can be estimated by boiling with alkali hydroxide solution and titrating the ammonia evolved. It also reacts with a solution of *p*-nitrobenzenediazonium chloride in the presence of an excess of sodium hydrogen carbonate, yielding a blood-red solution, which changes to yellow on the addition of a slight excess of acid; in acid solution a voluminous, yellow precipitate is obtained, which decomposes rapidly, yielding a resinous product free from sulphur.

Benzoyl chloride and alkali react with the ester, yielding benzoic anhydride, and a hot solution of the ester rapidly transforms phenylhydrazine into its *N*-sulphonic acid.

When boiled with alkalis, the ester yields ammonia, alkali sulphite, and glutaconaldehyde, the last of which was isolated as its dianilide, NPh:CH·CH:CH·CH:CH·NHPh (compare Zincke, Abstr., 1904, i, 448; Koenig, *ibid.*, i, 817), the hydrochloride of which crystallises in red needles, m. p. 141—143°.

When the ester is neutralised with sodium hydroxide solution, and then boiled with phenylhydrazine for three hours, ammonia is evolved, and the *sodium* salt of 1-*anilino*-2 : 4 : 6-*trihydroxypiperidine trisulphite*, $C_{11}H_{13}O_9N_2S_3Na_3,2H_2O$, is obtained as colourless crystals, which begin to decompose at 180°. J. J. S.

The Action of Sulphites on Pyridine. FRITZ REITZENSTEIN and WILHELM BREUNING (*Ber.*, 1910, **43**, 2939—2940. Compare Schenkel, preceding abstract).—A claim for priority. The existence of Zincke's glutaconaldehyde, which Schenkel has isolatad in the form of its dianilide, had already been demonstrated by the authors, who obtained from it the ditoluidide (Breuning, *Diss.*, Würzburg, 1909).

R. V. S.

Additive Compounds of Mercury Salts and Aromatic Bases. WILHELM STARONKA (*Bull. Acad. Sci. Cracow*, 1910, 372—398).—The great solubility of mercury salts in organic bases is due to the formation of additive compounds of the salts and the solvent. The salts of mercury which have been examined are the cyanide, chloride, bromide, and iodide; the bases used are aniline, pyridine, and quinoline. Exactly weighed amounts of a salt and a base are heated in a sealed tube until fusion is complete. The tube is allowed to cool until crystals, generally of an additive compound, separate, and is then carefully re-heated until only a pair of crystals remain; the temperature at which the two crystals persist unchanged for a long time is taken as the temperature of solidification of the mixture under examination. The results are expressed graphically, the molecular concentrations of one constituent being plotted as abscissæ, the corresponding temperatures of solidification as ordinates. The curves obtained are of two types, one kind exhibiting a maximum corresponding with the m. p. of the additive compound, and the other kind showing breaks, indicating the transition of one solid phase into another. The compositions of the additive compounds can be determined directly from curves of the first type. In the case of mixtures giving curves of the second type, it is necessary to isolate the solid phase before its composition can be determined by analysis. The isolation is a matter of some difficulty, because the solid phase is only stable within a definite range of temperature; a method is described by which the separation can be effected by the use of a centrifugaliser in an air-bath. Of the bases examined, pyridine shows the greatest tendency to form additive compounds; of the salts, the cyanide. The most frequently occurring types of additive compounds are $HgX_2,2B$ and HgX_2,B, where B = 1 mol. of the base. The following new additive compounds have been obtained: $Hg(CN)_2,6C_5NH_5$; $Hg(CN)_2,3C_5NH_5$; $2Hg(CN)_2,3C_5NH_5$; $Hg(CN)_2,C_5NH_5$; $HgBr_2,C_5NH_5$, m. p. 123°; $3HgBr_2,2C_5NH_5$, m. p. 134°; HgI_2,C_5NH_5, m. p. 90°; $Hg(CN)_2,3C_9NH_7$; $HgBr_2,2C_9NH_7$; $HgI_2,2C_9NH_7$; $Hg(CN)_2,4PhNH_2$ (metastable); $HgBr_2,PhNH_2$, m. p. 124°.

C. S.

Theories of the Constitution of Double Salts. PAUL PFEIFFER [with B. FRIEDMANN and H. REKATE] (*Annalen*, 1910, **376**, 310—344).—The constitution of the double salts formed by metallic halogenides has been explained by various theories, of which the Blomstrand-Remsen and the Werner are the most prominent. According to the former, the constitution is represented by, for example,

$\begin{matrix}Cl\\Cl\end{matrix}\!>\!P\!<\!\begin{matrix}Cl\dot{:}ClK\\Cl\dot{:}ClK\end{matrix}$, the addition occurring by means of tervalent halogen atoms, whilst the constitution is expressed by $[PtCl_6]K_2$ by the well-known Werner theory.

The following compounds have been prepared in order to differentiate between these two theories. They are double salts of tin halogenides, all of the type SnA_n, but containing different numbers of halogen atoms, and alkali halogenides or similar compounds. According to the Blomstrand-Remsen theory, the number of molecules of alkali halogenide added is a function of the number of halogen atoms in the tin halogenide; by the Werner theory the number added is independent of the number of halogen atoms in the tin halogenide. The existence of compounds, such as $SnPh_3Cl,2C_5NH_5,2HCl$ and

$SnPh_3Br,2C_5NH_5,2HBr$,

is contrary to the Blomstrand-Remsen theory.

Pyridinium stannichloride, $2Py,H_2SnCl_6$, obtained from pyridine and stannic chloride in concentrated hydrochloric acid, and *quinolinium stannichloride*, $2Qn,H_2SnCl_6$ ($Qn = C_9NH_7$), m. p. 266°, similarly prepared, form colourless crystals; the *stannibromides*, $2Py,H_2SnBr_6$ and $2Qn,H_2SnBr_6$, m. p. 258—261°, are yellow. Pyridinium stanni-iodide, $2Py,H_2SnI_6$, prepared from pyridine hydriodide and stannic iodide in alcoholic hydrogen iodide, forms dark brown leaflets (compare Rosenheim and Aron, Abstr., 1904, ii, 411. The substance described by these authors as forming bluish-black needles is pyridinium periodide, $HPyI_3$). *Pyridinium stannimethylpentachloride*, $[SnCl_5Me]2HPy$, and the *quinolinium* salt, $[SnCl_5Me]2HQn$, m. p. 200° (decomp.), obtained from methylstannic acid and pyridine or quinoline in cold concentrated hydrochloric acid, form colourless crystals. *Pyridinium stannimethylpentabromide*, $[SnBr_5Me]2HPy$, m. p. 165—172° (decomp.), and the *quinolinium* salt, $[SnBr_5Me]2HQn$, m. p. 80—145° (decomp.), obtained from alcoholic tin methyl bromide and pyridine or quinoline in concentrated hydrobromic acid, crystallise in yellow needles. Stannimethylpentaiodides cannot be prepared. *Pyridinium stannidimethyltetrachloride*, $[SnCl_4Me_2]2HPy$, m. p. 143—144°, and the *quinolinium* salt, $[SnCl_4Me_2]2HQn$, m. p. 167°, obtained from tin dimethyl chloride (m. p. 108°, not 90°) and pyridine or quinoline hydrochloride in methyl-alcoholic hydrogen chloride, form colourless needles. The corresponding *stannidimethyltetrabromide*, $[SnBr_4Me_2]2HPy$, m. p. 108—112°, and $[SnBr_4Me_2]2HQn$, m. p. 134°, prepared in a similar manner, are colourless, but gradually become yellow by keeping. The following six compounds are also prepared in a similar manner: $[SnCl_4Et_2]2HPy$, m. p. 118—122°, colourless prisms;

$[SnCl_4Et_2]2HQn$,

m. p. 134—135°, stable, colourless needles; $[SnBr_4Et_2]2HPy$, m. p. 90—99°, colourless needles; $[SnBr_4Et_2]2HQn$, m. p. 120—124°, colourless needles; $[SnCl_4Pr^{a}_2]2HPy$, m. p. 114°, colourless plates; $[SnBr_4Pr^{a}_2]2HPy$, m. p. 100—114°, colourless leaflets. *Pyridinium stannidiphenyltetrachloride*, $[SnCl_4Ph_2]2HPy$, m. p. 186°, obtained from stannic diphenyl oxide and pyridine hydrochloride in saturated methyl- or ethyl-alcoholic hydrogen chloride, and the *quinolinium* salt, $[SnCl_4Ph_2]2HQn$, m. p. 133—140°, similarly prepared, form colourless

crystals. The corresponding *bromo*-compounds, $[SnBr_4Ph_2]2HPy$, m. p. 195°, and $[SnBr_4Ph_2]2HQn$, m. p. 119—129° or 130—131° (different samples), are likewise colourless. *Pyridinium stannitri phenyltrichloride*, $[SnClPh_3]2HPy$, m. p. 169—170°, obtained from stannic triphenyl chloride (m. p. 112—113°, not 106°) and pyridine hydrochloride in methyl-alcoholic hydrogen chloride, and *pyridinium stannitriphenyltribromide*, $[SnBr_3Ph_3]2HPy$, m. p. 146—153° or, after resolidification, 194°, similarly prepared, form colourless crystals, and are the only substances which can be obtained from tin halogenides of the type SnR_3Cl. C. S.

Betaines of Pyridinium-maleic and Pyridiniumacrylic Acids and their Salts. PAUL PFEIFFER and A. LANGENBURG [in part with Miss BIRENCWEIG] (*Ber.*, 1910, **43**, 2926—2939. Compare O. Lutz, following abstract).—When dibromosuccinic acid is treated with pyridine, a mixture of pyridine salts is obtained, which, on warming, evolves carbon dioxide, and leaves a residue from which two substances can be isolated. Of these, one contains ionic bromine, has acid properties, and is identical with the compound obtained from pyridine and α-bromoacrylic acid. To it is therefore ascribed the structure of α-pyridiniumacrylic acid bromide, $C_5H_5NBr\cdot C(:CH_2)\cdot CO_2H$. The other substance yields an additive product with hydrogen bromide, which, on heating, loses carbon dioxide and is converted into α-pyridiniumacrylic acid bromide, so that it probably has the structure of a betaine of pyridinium-maleic acid, $\begin{array}{l} C_5H_5\underset{|}{N}\cdot\underset{|}{C}:CH\cdot CO_2H \\ \quad\quad\; O\cdot CO \end{array}$ or

$\begin{array}{l} C_5H_5\cdot \underset{|}{N}\text{——}\underset{||}{C}\cdot CO_2H \\ \quad\quad\; O\cdot CO\cdot CH \end{array}$, the maleic structure being more probable than the fumaric, because quinoline and dibromosuccinic acid yield quinoline bromomaleate. The salts described give with alkalis yellow solutions, becoming blood-red (compare the colour reactions of dinitrophenyl pyridinium salts: Zincke, Abstr., 1907, i, 625).

Dibromosuccinic acid and excess of pyridine on standing for two days at the ordinary temperature yield the *tripyridine* salt,

$$CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H,3C_5H_5N,$$

as a white powder, which when kept over sulphuric acid loses pyridine, forming the *monopyridine* salt, $C_4H_4O_4Br_2\cdot C_5H_5N$, which after crystallisation forms colourless needles, m. p. about 143° (with evolution of gas).

Pyridine bromomaleate, $C_4H_3O_4Br,C_5H_5N$ (from bromomaleic acid in ethereal solution), is a white, crystalline precipitate, m. p. 94—100°. *Pyridine bromofumarate*, $C_4H_3O_4Br,C_5H_5N$, may be prepared in the same way.

Quinoline bromomaleate, $C_4H_3O_4Br,C_9H_7N$, is obtained on heating dibromosuccinic acid for some hours with quinoline; it forms colourless needles, m. p. 114—115° (with evolution of gas), and yields bromomaleic acid on treatment with ammonia.

The *betaine* of *pyridinium-maleic acid* is obtained by heating dibromosuccinic acid with pure pyridine for one hour at 60—70°. The

α-pyridiniumacrylic acid bromide, which is also produced, is removed by the addition of a little water, in which it is very soluble. The betaine becomes brown at 195°. Sodium carbonate dissolves it with evolution of carbon dioxide. When the substance is dissolved in concentrated hydrochloric acid and evaporated on the water-bath, *pyridiniummaleic acid chloride*, $C_5H_5NCl\cdot C(CO_2H){:}CH\cdot CO_2H$, is obtained; it crystallises in small white colourless tablets, which decompose at 150° with evolution of gas, having become brown a few degrees previously. The *bromide* may be obtained similarly, or, better, (1) by adding the betaine to concentrated hydrobromic acid until the salt separates out; (2) by evaporating over soda-lime a solution of the betaine in concentrated hydrobromic acid. It forms colourless, prismatic crystals, which decompose at 170°. On heating it to 110°, α-pyridiniumacrylic acid bromide is obtained.

α-Pyridiniumacrylic acid bromide is also obtained by warming pyridine with dibromosuccinic acid (*v.s.*), bromomaleic acid, bromofumaric acid, αβ-dibromopropionic acid, or α-bromoacrylic acid. It forms colourless needles, m. p. 216° (decomp.). With moist silver oxide it gives the betaine in solution. It gives precipitates with potassium dichromate, gold and platinum solutions. *α-Pyridiniumacrylic acid chloride*, $C_8H_8O_2NCl,H_2O$, is prepared from the bromide by the action of moist silver oxide followed by hydrochloric acid; it forms colourless needles, m. p. 195° (decomp.). The *platinochloride*,

$$(C_8H_8O_2N)_2PtCl_4,4H_2O,$$

darkens on heating, and decomposes at 196°. The *platinichloride*, $(C_8H_8O_2N)_2PtCl_6,4H_2O$, decomposes at 200°. The *picrate*,

$$C_8H_8O_2N\cdot O\cdot C_6H_2(NO_2)_3,$$

has m. p. about 158° (decomp.). R. V. S.

Characteristic Reaction of Maleic Acid. OSCAR LUTZ (*Ber.*, 1910, **43**, 2636—2641).—Anhydropyridiniumsuccinic acid (pyridineaminosuccinic acid, Abstr., 1901, i, 8) is also formed when *dl*-bromosuccinic acid is treated with pyridine under the conditions described by Dubreuil (Abstr., 1904, i, 189), and is the substance described by Dubreuil as pyridine hydrogen fumarate. The anhydro-compound can also be obtained from maleic acid, for example, (*a*) when pyridine hydrogen maleate is heated at its melting point (105°) for 15—20 minutes; (*b*) by keeping an aqueous-alcoholic or methyl-alcoholic solution of pyridine and maleic acid at the ordinary temperature for several weeks.

Anhydropyridiniumsuccinic acid, $C_5H_5N{<}\begin{matrix}CH(CO_2H)\cdot CH_2\\ \text{———}O\cdot CO\end{matrix}$ or $C_5H_5N{<}\begin{matrix}O\cdot CO\\ \text{—}CH\cdot CH_2\cdot CO_2H\end{matrix}$, has m. p. 192°, and its solubility in water at 18° is 1·65.

This reaction of maleic acid with pyridine is used as an argument in favour of the structural formula $CO_2H\cdot CH{<}\begin{matrix}O\text{—}\\ CH_2\end{matrix}{>}CO$, for maleic acid. J. J. S.

Conversion of Hydrogenised Carbazoles into Derivatives of 2-Aminodiphenyl. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 2879—2881).—In the form of their benzoyl derivatives, the hexahydrocarbazole compounds obtained by the reduction of the corresponding tetrahydrocarbazoles, prepared from *cyclo*hexanones by Fischer's indole synthesis, are readily ruptured by phosphorus pentachloride. Thus hexahydrocarbazole is converted into its *benzoyl* derivative, b. p. about 270°/10 mm., which yields 20—25% of 2-benzoylaminodiphenyl when heated with phosphorus pentachloride, first on the water-bath and finally at 120°. In a similar manner, 1-benzoyl-4-methylhexahydrocarbazole yields *2-benzoylamino-4′-methyldiphenyl*, $C_6H_4Me\cdot C_6H_4\cdot NHBz$, m. p. 122°. C. S.

Tricyclic Quinolines. WALTHER BORSCHE [with R. SCHMIDT, H. TIEDTKE, and W. ROTTSIEPER] (*Annalen*, 1910, **377**, 70—123).—Quinoline derivatives containing a third ring condensed on the pyridine nucleus in positions 2 : 3 or 3 : 4 have been prepared by the three following methods: 1. Condensation of primary arylamines with semicyclic ketones obtained from alicyclic ketones and esters. 2. Condensation of alicyclic ketones containing the grouping $\cdot CO\cdot CH_2\cdot$ with *o*-acylanilides. 3. Condensation of isatic acid with alicyclic ketones to acids of the desired bases, and subsequent elimination of carbon dioxide.

The products, for example, $C_6H_4<\begin{array}{l}CH:C\cdot CH_2\\ N{=}C\cdot CH_2\end{array}>CH_2$ and

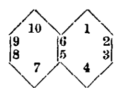
$$C_6H_4<\begin{array}{l}CH:C\cdot CH_2\cdot CH_2\\ N{=}C\cdot CH_2\cdot CH_2\end{array}>CH_2,$$

are regarded as 2:3-disubstituted quinolines, and are termed 2 : 3-trimethylenequinoline and 2 : 3-pentamethylenequinoline. The corresponding tetramethylene compounds are regarded as derived from tetrahydroacridine.

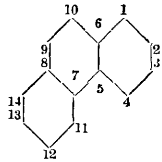
The general nomenclature of cyclic systems is discussed. The Greek capitals *gamma* Γ, *tau* T, and *pi* Π are suggested for a bridge, an acetylene linking, and a diagonal linking respectively; pinene is thus 1-methyl-$\Gamma^{2(4)}$-dimethylmethylene-$\Delta^{1(6)}$-*cyclo*hexene, camphane is 1-methyl-$\Gamma^{1(4)}$-dimethylmethylene*cyclo*hexane, tropan is $\Gamma^{1(4)}$-methylimino*cyclo*heptane, thujone is 1-methyl-4-*iso*propyl-$\Pi^{4(6)}$*cyclo*hexan-2-one, and Moycho and Zienkowski's tricyclene (Abstr., 1905, i, 711) is 1 : 1-dimethyl-$\Gamma^{2(5)}$-methylene-$\Pi^{5(7)}$-*cyclo*heptane.

The following considerations are of importance in the numbering of the atoms of ring systems. 1. The system should indicate as far as possible the analogies in the structure of closely related compounds, for example, anthracene, xanthen, and acridine, phenanthrene and phenanthridine, etc. 2. The system should admit a numbering of the analogous reduced cyclic compounds without any alterations in the relative numbering of the substituents. The conditions would be fulfilled by the following system. The cyclic system is so written that as many directly condensed rings as possible lie on a straight line. *Each* atom of a ring system is numbered, including, for example (unlike the system adopted in Richter's Lexikon der Kohlenstoff-Verbindungen), the carbon atoms common to two rings in the naphthalene, anthracene, and similar systems.

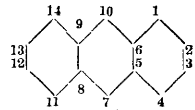
The numbering begins at the top of the ring on the extreme right (that is, the atom in the ortho-position to the second ring), and each atom of the first ring is numbered before proceeding to the second ring; for example:



Naphthalene.



Phenanthrene.



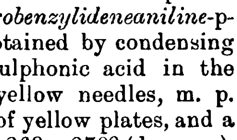
Acridine.

[This re-numbering is not followed in the abstract.]

Hydroxymethylene*cyclo*hexanone (Wallach, Abstr., 1904, i, 105) is best prepared by the action of sodium wire on a mixture of *cyclo*hexanone and *iso*amyl formate. It has b. p. 87°/14 mm., and tends to resinify when kept. With aniline, it yields *a-ketohexahydrobenzylidene aniline*, $CH_2<^{CH_2\cdot CH_2}_{CH_2\cdot CO}>CH\cdot CH:NPh$, which crystallises from alcohol in yellow needles, m. p. 154°. Heating with concentrated sulphuric acid transforms this compound into *a-ketohexahydrobenzylideneaniline*-p-*sulphonic acid*, $C_{13}H_{15}O_4NS$, which can also be obtained by condensing hydroxymethylene*cyclo*hexanone with aniline-*p*-sulphonic acid in the presence of *N*-potassium hydroxide. It forms yellow needles, m. p. 261—262°, yields an *ammonium* salt in the form of yellow plates, and a *potassium* salt in the form of rhombic crystals, m. p. 269—270° (decomp.).

a-Ketohexahydrobenzylidene-m-*aminophenol*, $C_{13}H_{15}O_2N$, prepared by condensing the components in glacial acetic acid solution, crystallises in yellow needles, m. p. 172—173°. Neither of the above condensation products yields a quinoline derivative.

*Acetyl*cyclo*hexan-2-one*, $CH_2<^{CH_2-CO}_{CH_2-CH_2}>CHAc$, prepared by the condensation of *cyclo*hexanone and ethyl acetate with sodium, is best isolated as its *copper* derivative in the form of a greenish-grey, crystalline powder, m. p. 160—161°. The free ketone is a colourless oil with b. p. 97—98°/11 mm., and can be kept for some time. It condenses with *m*-aminophenol in glacial acetic acid solution, yielding the m-*hydroxyanil*, $OH\cdot C_6H_4\cdot N:C_6H_9Ac$, as yellow needles, m. p. 186—187°, which react with concentrated sulphuric acid at 100°, yielding the quinoline derivative, 5-*methyl*-8-*hydroxy*-1:2:3:4-*tetrahydroacridine* (5-*methyl*-7-*hydroxy*-2 : 3-*hexamethylenequinoline*: annexed formula). The *sulphate* crystallises from dilute alcohol in yellowish-white needles, m. p. 225°, and the free base crystallises in glistening plates, which darken at 240°, but are not completely molten at 360°; its solutions have a yellowish-green fluorescence.



Aniline and *d*-4-acetyl-1-methyl*cyclo*hexan-3-one react at 150°, yielding a mixture of isomeric anils, $COMe\cdot C_6H_8Me:NPh$ and

$$OH\cdot C_6H_7Me\cdot CMe:NPh,$$

or the tautomeric enolic forms. A mixture of the two has b. p.

211°/14 mm., and cannot be separated; the mixture, when heated for three hours with concentrated sulphuric acid on the water-bath, yields a mixture of the two quinoline bases, $C_{15}H_{17}N$, namely:

$$C_6H_4{<}\begin{matrix}CMe{:}C\cdot CH_2\cdot CH_2 \\ N = C\cdot CH_2\cdot CHMe\end{matrix} \quad \text{and} \quad \begin{matrix}N{:}CMe\cdot C\cdot CH_2\cdot CH_2 \\ C_6H_4 - C\cdot CH_2\cdot CHMe\end{matrix}.$$

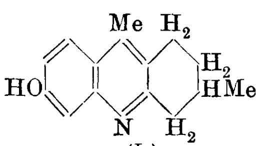
d-2 : 5-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine*. d-6 : 9-*Dimethyl*-5 : 6 : 7 : 8-*tetrahydrophenanthridine*.

A mixture of the two has b. p. 200°/14 mm., and the separation is based on the fact that the former yields a sparingly soluble hydrochloride and the latter a sparingly soluble dichromate. The acridine base crystallises from light petroleum in colourless needles, m. p. 72—74°, and $[\alpha]_D$ +57·07°. Its solutions in acids have a greenish-yellow fluorescence. The *picrate* forms a yellow, crystalline powder, m. p. 193°; the *methiodide*, $C_{16}H_{20}NI$, crystallises from alcohol in yellow needles, m. p. 232—233°; the *platinichloride*,

$$2C_{15}H_{17}N_2,H_2PtCl_6,$$

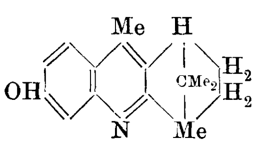
forms orange-coloured needles, m. p. 213—223°, and the *aurichloride*, $2C_{15}H_{18}NCl,AuCl_3$, yellow needles, m. p. 166°. The same base can also be prepared by condensing *o*-aminoacetophenone with *d*-3-methyl*cyclo*hexanone, and when distilled with zinc dust in an atmosphere of hydrogen yields 2 : 5-*dimethylacridine*, $C_{15}H_{13}N$, colourless needles, m. p. 121—122°, the *picrate* of which is sparingly soluble in hot alcohol and has m. p. 225°. A by-product is 2 : 5-*dimethyl*-5 : 10-*dihydroacridine*, $C_{15}H_{15}N$, which crystallises from alcohol in colourless plates, m. p. 165—166°.

The dimethyltetrahydrophenanthridene crystallises from light petroleum, has m. p. 78° and $[\alpha]_D$ +133·7°, and its solutions in acids do not fluoresce. The *picrate* has m. p. 208° (decomp.); the *aurichloride*, $C_{15}H_{17}N,HAuCl_4$, crystallises in yellow needles, m. p. 128°. 9 : 10-*Dimethylphenanthridene*, $C_{15}H_{13}N$, is a colourless oil, and yields a *picrate*, m. p. 214°.



(I.)

d-1-*Methyl*-4-*acetyl*cyclo*hexan*-3-*one*-m-*hydroxyanil*, $OH\cdot CMe{:}C_6H_7Me{:}N\cdot C_6H_4\cdot OH$, obtained from *m*-aminophenol and *d*-1-methyl-4-acetyl*cyclo*hexan-3-one, separates from alcohol in yellow, crystalline aggregates, m. p. 153—154°, and with sulphuric acid yields 2 : 5-*dimethyl*-8-*hydroxy*-1 : 2 : 3 : 4-*tetrahydroacridine* (formula I). This forms greenish-yellow crystals, m. p. 272—273°, and yields a *sulphate* in the form of colourless needles, m. p. 207—208°. When distilled with zinc dust in an atmosphere of hydrogen, the base yields 2:5-dimethylacridine.



(II.)

d-α-*Acetylcamphor*-m-*hydroxyanil*, $C_{10}H_{15}Ac{:}N\cdot C_6H_4\cdot OH$, crystallises from alcohol in colourless, flat needles, m. p. 151—152°, and with concentrated sulphuric acid yields the quinoline *base*, $C_{18}H_{21}ON$ (formula II). This crystallises in yellow needles, which are unaltered at 360°, and yields a *picrate*.

1 : 2 : 3 : 4-*Tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_4<\underset{N}{\overset{C(CO_2H)}{\rule{3em}{0.4pt}}}>C_6H_8,$$

prepared by condensing *cyclo*hexanone with isatin in the presence of 33% potassium hydroxide and alcohol, crystallises in colourless, glistening plates, m. p. 284—286° (decomp.). The *picrate* forms yellow needles, m. p. 199·5° (decomp.); the *aurichloride*,

$$(C_{14}H_{13}O_2N,HCl)_3,2AuCl_3,10H_2O,$$

has m. p. 237° (decomp.); the *platinichloride*,

$$2C_{14}H_{13}O_2N,H_2PtCl_6,6H_2O,$$

forms glistening, brown crystals, m. p. 222—223°; and the *methyl* ester, $C_{13}H_{12}N{\cdot}CO_2Me$, prepared from the silver salt, has b. p. 200°/20 mm. and m. p. 70°; it yields a *picrate*, m. p. 176—178°, and a *platinichloride*, as red needles, m. p. 204—208°; the *ethyl* ester,

$$C_{13}H_{12}N{\cdot}CO_2Et,$$

forms broad needles, m. p. 55°, and yields a *picrate*, m. p. 166—167°, a *platinichloride*, $2C_{16}H_{17}O_2N,H_2PtCl_6$, m. p. 193—194°, and an *ethiodide*, $C_{18}H_{22}O_2NI$, m. p. 168°. 1 : 2 : 3 : 4-Tetrahydroacridine, prepared by heating the carboxylic acid at its m. p., yields a *sulphate*, with m. p. 148°, and a *mercurichloride*, in the form of colourless needles, m. p. 213—214°. The base condenses with benzaldehyde and zinc chloride at 160—170°, yielding 1-*benzylidene*-1 : 2 : 3 : 4-*tetrahydroacridine*,
$C_6H_4<\begin{matrix}C{=}C{\cdot}CH_2{-}{-}{-}CH_2\\ N{=}C{\cdot}C(:CHPh){\cdot}CH_2\end{matrix}$, which crystallises from dilute alcohol in glistening plates, m. p. 103—104°. Its *picrate* has m. p. 176—178°. Tetrahydroacridine and phthalic anhydride yield a *phthalone*. When nitrated with 10% nitric acid, the tetrahydro-base yields a mixture of two *nitro*-derivatives, $C_{13}H_{12}N{\cdot}NO_2$, namely, dark yellow prisms, melting at 126—130°, and yellow needles, m. p. 138—139°, which have to be separated mechanically. With fuming sulphuric acid at 100°, the base yields *tetrahydroacridine*-6-*sulphonic acid*, $C_{13}H_{13}O_3NS$, which crystallises from water in colourless prisms, but at 130—140° the chief product is an isomeric *sulphonic acid*, m. p. 248—250°, together with a small amount of the above sulphonic acid, which is not molten at 300°, and of a *disulphonic acid*.

The base reacts with bromine, yielding the *hydrobromide perbromide* $C_{13}H_{13}N,HBr_3$, as yellowish-red needles, m. p. 123°.

7-*Bromo*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_3Br<\underset{N}{\overset{C(CO_2H)}{\rule{3em}{0.4pt}}}>C_6H_8,$$

prepared from *cyclo*hexanone, 5-bromoisatin, and alkali, crystallises in minute needles, m. p. 274—276°, after drying at 120°. When heated at its m. p., the acid yields 7-*bromotetrahydroacridine*, $C_{13}H_{12}NBr$ which crystallises from alcohol in flat needles, m. p. 93—94°. The *picrate* crystallises in greenish-yellow plates, m. p. 194—195°, and the *aurichloride* in microscopic needles, m. p. 208°. 7 : 9-*Dibromo*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*, $C_{14}H_{11}O_2NBr_2$, prepared from 3 : 5-dibromoisatin, crystallises in broad needles, m. p. 242°. 7 : 9-*Dibromotetrahydroacridine*, $C_{13}H_{11}NBr_2$, crystallises in yellow needles, m. p. 105—107°.

d-2-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_4<\begin{matrix}C(CO_2H):C\cdot CH_2\cdot CH_2\\ \text{———}N:C\cdot CH_2\cdot CHMe\end{matrix},$$

obtained from isatin and *d*-1-methyl*cyclo*hexan-3-one, crystallises from glacial acetic acid in yellow needles, m. p. 291—293° (decomp.). d-2-*Methyltetrahydroacridine*, $C_{14}H_{15}N$, crystallises from light petroleum in colourless, slender plates, m. p. 81—82°, and yields a *picrate*, m. p. 176—177°. The corresponding *dl*-base has m. p. 72—73°, and both the *d*- and the *dl*-base when heated with lead oxide yield 3-methylacridine, the *dichromate* of which forms red needles, m. p. 125—126°.

Isatin and 1-methyl*cyclo*hexan-4-one yield 3-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridine*-5-*carboxylic acid*,

$$C_6H_4<\begin{matrix}C(CO_2H):C\cdot CH_2\cdot CHMe\\ \text{———}N:C\cdot CH_2\cdot CH_2\end{matrix},$$

in the form of yellow needles, m. p. 280—281°. 3-*Methyltetrahydroacridine*, $C_{14}H_{15}N$, crystallises from light petroleum in quadratic plates, m. p. 84—85°, and yields a *picrate*, m. p. 194—195°. When heated with lead oxide, the base yields 3-methylacridine (Ullmann, Abstr., 1888, 288).

Pulegone and isatin in the presence of concentrated potassium hydroxide yield α-methylcinchonic acid, together with neutral products, probably owing to the conversion of the pulegone into acetone and 1-methyl*cyclo*hexan-3-one.

2 : 3-*Trimethylenecinchonic acid*, $C_6H_4<\begin{matrix}C(CO_2H):C\cdot CH_2\\ \text{———}N:C\cdot CH_2\end{matrix}>CH_2$, obtained from isatin, *cyclo*pentanone, and alkali, crystallises from alcohol or glacial acetic acid in small needles, m. p. 277—278° (decomp.). 2 : 3-*Trimethylenequinoline*, $C_{12}H_{11}N$, formed when the acid is heated at its m. p. or by condensing *cyclo*pentanone with *o*-aminobenzaldehyde, crystallises from light petroleum in colourless needles, m. p. 59—60° ; the *dichromate* forms sparingly soluble, orange, yellow prisms; the *picrate*, pale yellow needles, m. p. 203—204°; the *aurichloride*, $C_{12}H_{11}N,HAuCl_4$, needles, m. p. 160—162°; the *platinichloride*, reddish-yellow needles, m. p. 235°; and the *methiodide*, $C_{13}H_{14}NI$, pale yellow crystals, m. p. 207°.

2 : 3-*Pentamethylenecinchonic acid*,

$$C_6H_4<\begin{matrix}C(CO_2H):C\cdot CH_2\cdot CH_2\\ \text{———}N:C\cdot CH_2\cdot CH_2\end{matrix}>CH_2,$$

crystallises from glacial acetic acid in glistening needles, m. p. 291—292°, and 2 : 3-*pentamethylenequinoline*, $C_{14}H_{15}N$, from light petroleum in colourless needles, m. p. 93·5°; its *hydrochloride* forms broad needles, m. p. 107—108°; its *picrate*, yellow needles, m. p. 197°; its *methiodide* has m. p. 195—196° ; its *aurichloride*,

$$C_{14}H_{15}N,HAuCl_4,$$

forms yellow needles, m. p. 179°, and its *platinichloride* crystallises with $2H_2O$ in orange-red needles, m. p. 214°. J. J. S.

Oxazole Series. Syntheses of 2-Ketotetrahydro-oxazoles. TREAT B. JOHNSON and RALPH W. LANGLEY (*Amer. Chem. J.*, 1910, **44**, 352—361).—Nemirowsky (Abstr., 1885, 741) has shown that

carbonyl chloride reacts with β-chloroethyl alcohol at 200° to form β-chloroethyl chloroformate. When this ester was treated with aniline, chloroethyl phenylcarbamate, $CH_2Cl\cdot CH_2\cdot O\cdot CO\cdot NHPh$, was produced, and was converted by alkali hydroxide into 2-keto-3-phenyl-tetrahydro-oxazole, $O<\begin{matrix}CO-NPh\\ CH_2\cdot CH_2\end{matrix}$. Otto (Abstr., 1891, 1373) studied the action of carbonyl chloride on the dichlorohydrins, and obtained acid chlorides, from which he prepared a series of urethanes. He found that the urethanes from $\alpha\alpha$-dichlorohydrin yielded ketotetrahydro-oxazoles when they were treated with alkali hydroxide, whilst those from $\alpha\beta$-dichlorohydrin did not behave in this way. In view of these results, a study has now been made of various halogenalkyl phenylcarbamates and their behaviour towards alkali hydroxide.

$\beta\beta$-Dichloroisopropyl phenylcarbamate, $CH(CH_2Cl)_2\cdot O\cdot CO\cdot NHPh$, m. p. 73°, obtained by the action of phenylcarbimide on $\alpha\alpha$-dichlorohydrin at 100°, crystallises in groups of slender needles, and when heated with potassium hydroxide is converted almost quantitatively into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole,

$$O<\begin{matrix}CO-\!\!-\!\!-\!\!-NPh\\ CH(CH_2Cl)\cdot CH_2\end{matrix}$$

(Otto, *loc. cit.*).

$\beta\beta'$-Chlorobromoisopropyl phenylcarbamate, m. p. 73°, obtained by the interaction of phenylcarbimide and $\beta\beta'$-chlorobromo*iso*propyl alcohol, crystallises in needles, and is converted by potassium hydroxide into 2-keto-3-phenyl-5-chloromethyltetrahydro-oxazole.

β-Chloro-γ-bromopropyl phenylcarbamate, m. p. 73°, was prepared from phenylcarbimide and β-chloro-γ-bromopropyl alcohol. *γ-Chloro-β-bromopropyl phenylcarbamate*, m. p. 75—76°, is converted by potassium hydroxide into *2-keto-3-phenyl-4-chloromethyltetrahydro oxazole*,

$$O<\begin{matrix}CO-NPh\\ CH_2\cdot CH(CH_2Cl)\end{matrix},$$

m. p. 73—78°, which forms groups of needles. A small yield of this oxazole was also obtained by the action of potassium hydroxide on $\beta\beta'$-dichloropropyl phenylcarbamate. *$\beta\beta'$-Dibromoisopropyl, $\beta\gamma$-dichloropropyl*, and *$\beta\gamma$-dibromopropyl phenylcarbamates* have m. p. 73°, 72—73°, and 77—79° respectively. E. G.

Oxazole Series: the Addition of Cyanic Acid to Epichlorohydrin. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1910, **44**, 5, 453—466).—Thomsen (Abstr., 1879, i, 217) has described the formation of a ketotetrahydro-oxazole, $C_4H_6O_2NCl$, from the action of potassium cyanate on epichlorohydrin. The authors have synthesised this substance by the action of strong alkali on $\beta\beta'$-dichloro*iso*propyl acetylcarbamate, and thus determined the manner of addition of cyanic acid to epichlorohydrin. It is shown that theoretically three isomeric cyclic compounds might be formed by this addition: 2-keto-5-chloromethyltetrahydro-oxazole, 2-keto-4-chloromethyltetrahydro-oxazole, and γ-chloropropylene iminocarbonate, and that the substance formed must be assigned the structure of the first of these.

ββ'-Dichloroisopropyl acetylcarbamate, $NHAc\cdot CO_2\cdot CH(CH_2Cl)_2$, crystallises in needles, m. p. 100°.

ββ'-Dichloroisopropyl benzoylcarbamate crystallises in rectangular prisms, m. p. 119°. *2-Keto-3-phenylcarbamyl-5-chloromethyltetrahydro-oxazole*, $CH_2Cl\cdot CH<\begin{matrix}O\text{—}CO\\ CH_2\cdot N\cdot CO\cdot NHPh\end{matrix}$, forms rhombic tablets, m. p. 154—155°; the corresponding *3-benzoylcarbamyl* derivative melts at 131—132°.

β-γ-Dichloropropyl acetylcarbamate forms prisms, m. p. 64—65°.

Allyl acetylcarbamate crystallises in flat prisms, m. p. 64°.

γ-Chloro-β-bromopropyl acetylcarbamate crystallises in prisms, m. p 60°. *γ-Chloro-β-bromopropyl carbamate* forms plates, m. p. 93°. *β-β'-Dibromoisopropyl benzoylcarbamate* crystallises in plates, m. p. 119°; the *β-chloro-β-bromo*-derivative melts at 122°.

β-γ-Dichloropropyl benzoylcarbamate and the corresponding *di-bromo*-derivative melt at 83°.

γ-Chloro-β-bromopropyl benzoylcarbamate forms tabular crystals, m. p. 113°.

β-Chloro-γ-bromopropyl benzoylcarbamate crystallises in prisms, m. p. 114°. N. C.

Diphenylene-sultam. FRITZ ULLMANN and CHRISTIAN GROSS (*Ber.*, 1910, **43**, 2694—2704).—A sultam could not be obtained from toluene-*p*-sulpho-3-nitro-*p*-toluidide, but one was prepared from *o*-nitro-benzenesulphonanilide, the reduction product of which,

$$NH_2\cdot C_6H_4\cdot SO_2\cdot NHPh,$$

was diazotised, and on the addition of sodium acetate formed *1-phenyl-benzsulphontriazine*, $C_6H_4<\begin{matrix}SO_2\cdot NPh\\ N{=}N\end{matrix}$; this was converted by sodium hydroxide and copper into *diphenylene-sultam*,

$$C_6H_4<\begin{matrix}SO_2\\ C_6H_4\end{matrix}>NH.$$

Phenylenenaphthylene-sultam was prepared in a similar manner. Both sultams are colourless, crystalline compounds of strongly acid character. The ring is not opened on heating with hydrochloric acid even under pressure.

Nitro-p-*toluenesulphonyl*-3 : 5-*dinitro*-p-*toluidide*, prepared by nitration of *p*-toluenesulphonyl-*p*-toluidide, crystallises in colourless prisms, m. p. 184°. Sulphuric acid converts it into 3 : 5 dinitro-*p*-toluidine. With methyl sulphate, p-*toluenesulphonylmethyl*-3 : 5-*dinitro*-p-*toluidide* is formed in faintly yellow crystals, m. p. 199°.

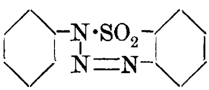
p-*Toluenesulphonyl-3-nitro*-p-*toluidide,* produced on nitrating with 18% nitric acid at 60—70°, forms yellow prisms, m. p. 101°. It yields 3-nitro-*p*-toluidine when hydrolysed. When reduced with stannous chloride, p-*toluenesulphonyltolylene*-3 : 4-*diamine* is obtained; it crystallises in needles, m. p. 140°; the *hydrochloride* forms colourless, silky needles, decomp. 170°. p-*Toluenesulphonylazimino-toluene* forms colourless needles, m. p. 159°. p-*Toluenesulphonyl-methyl-3-nitro*-p-*toluidide* has m. p. 124°. p-*Toluene sulphonylmethyl-3-amino*-p-*toluidide* forms colourless, matted needles, m. p. 133°.

Di-p-*toluenesulphonyl*-3-*nitro*-p-*toluidide* forms colourless needles, m. p. 228°; reduction converts it into *di*-p-*toluenesulphonyl-tolylene diamine*, crystallising in colourless needles, m. p. 192°.

o-*Nitrobenzenesulphonanilide* has m. p. 115°; o-*aminobenzenesulphonanilide* forms matted needles, m. p. 122°; the *hydrochloride* separates in colourless needles.

Diphenylene-sultam crystallises in well-formed, colourless, lustrous needles, m. p. 196°; it dissolves in ammonia and alkalis with a faint yellow coloration and bluish fluorescence. The mother liquors of the preparation contain *hydroxybenzenesulphonanilide*, colourless needles, m. p. 123°.

1-*Phenylbenzsulphontriazine* (annexed formula) is amorphous, m. p. 111° (decomp.). The triazine ring is immediately opened by dilute mineral acids, and the clear solutions couple with β-naphthol, forming red azo-dyes.



Diphenylene-N-*methylsultam* is obtained from *nitrobenzene sulphonmethylanilide*, m. p. 73°, which is reduced by stannous chloride to *aminobenzenesulphonmethylanilide*, forming colourless crystals, m. p. 63°. The last substance when diazotised, and the diazonium solution evaporated, gives the *sultam* in colourless needles, m. p. 112°.

o-*Nitrobenzenesulphonyl*-β-*naphthalide* forms colourless needles, m. p. 138°; on reduction, o-*aminobenzenesulphonyl*-β-*naphthalide* is formed, crystallising in needles, m. p. 113°.

1-β-*Naphthyl-benzsulphontriazine*, $C_6H_4<\begin{matrix}N{=}N\\ | \\ SO_2\cdot N\cdot C_{10}H_7\end{matrix}$, separates in colourless needles, m. p. 107—108°.

Phenylenenaphthalene-sultam, $C_6H_4<\begin{matrix}SO_2\\ C_{10}H_6\end{matrix}>NH$, crystallises in colourless needles, m. p. 254°; the solutions fluoresce faintly blue.

E. F. A.

Isomerism of Complex Compounds. I. Asymmetric Complex Compounds of Platinum. IWAN OSTROMISSLENSKY and AUGUST BERGMANN (*Ber.*, 1910, **43**, 2768—2774; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 611—624).—The object of the authors was to prepare complex compounds of platinum of the type $\begin{matrix}a\\ b\end{matrix}>Pt<\begin{matrix}m\\ n\end{matrix}$ or $\left[\begin{matrix}a\\ b\end{matrix}>Pt<\begin{matrix}m\\ n\end{matrix}\right]m_2$ in order to see if optical isomerides are capable of existence. If this were so it would follow that Werner's explanation of the existence of two isomerides of the formula $Cl_2Pt(NH_3)_2$ is not a correct one. The stable, asymmetric compound, cis-*plato-pyridine-ammine-chlorosulphite*, $\begin{matrix}Cl\\ HO_3S\end{matrix}>Pt<\begin{matrix}NH_3\\ NC_5H_5\end{matrix}$, has been prepared, but so far no evidence of isomerism has been obtained.

To prepare the above compound, sulphur dioxide is passed into an aqueous suspension of plato-semipyridine-ammine-chloride (Abstr., 1886, 857) heated on the water-bath. The ammine-chloride dissolves, leaving undissolved a small quantity of a yellow substance (*A*). The filtrate, on concentration, gives clear, colourless, monoclinic crystals

[$a:b:c = 0.966:1:0.712$; $\beta = 91°43'$] of the plato-pyridine-ammine-chlorosulphite. With brucine it gives an easily soluble salt or double compound.

The mother liquors from the chlorosulphite sometimes deposit a yellow substance, which is identical with *A*. It is soluble in chloroform, and can thus be separated from the chlorosulphite, which is practically insoluble. It contains the same percentage of platinum and nitrogen as the chlorosulphite, but it is not isomeric or identical with it, as it does not contain sulphur. A formula is not given for it.

Plato-semitolylenediamine chloride, $[Cl_2Pt(NH_2)_2\colon C_6H_3\cdot CH_3]$, was obtained by warming potassium platinochloride with 1 : 3 : 4-tolylenediamine. It forms microscopic, yellow needles, with a green tinge, which are insoluble in ordinary solvents. Attempts to prepare an asymmetric complex from it by replacing one of the chlorine atoms by the SO_3H group were not successful. Treatment with sulphites, bisulphites, or sulphur dioxide gave precipitates which were analysed, but to which the authors assign no formula.

Plato-semi*iso*butylenediamine chloride, as also the asymmetric compound, $\left[\begin{matrix}H_2C\cdot NH_2\\ |\\ Me_2C\cdot NH_2\end{matrix}\!\!>\!Pt(NH_2)_2\colon C_6H_3CH_3\right]$, are not capable of existence.

T. S. P.

Nitrosohydrazines, *iso*Azotates [*iso*Diazo-compounds], and Azo-compounds of the Aliphatic Series. JOHANNES THIELE (*Annalen*, 1910, **376**, 239—268; Abstr., 1908, i, 927).—The main object of the paper is to show that aliphatic *iso*azotates (*iso*diazo-compounds) behave like their aromatic analogues, except, of course, that they do not yield diazonium salts with acids.

The production of *iso*diazo-compounds from a primary hydrazine (or its nitroso-derivative, which has an asymmetric structure), ethyl nitrite, and sodium ethoxide is represented by the scheme: $NHR\cdot NH_2 \longrightarrow N(NO)R\cdot NH_2 \longrightarrow N(NO)R\cdot NH\cdot NO \longrightarrow N_2O + NHR\cdot NO$ (a decomposition resembling that of *sec.-as*-hydrazines by nitrous acid) $\longrightarrow RN\colon N\cdot ONa$. (The formation of Hantzsch and Lehmann's azotates, which are quite different from the *iso*azotates, from nitrosoalkylurethanes and very concentrated potassium hydroxide is explained by the intermediate formation of the same primary nitrosoamine, $NHR\cdot NO$. Further research is necessary in order to explain the remarkable difference in the course of the two reactions.)

Methylhydrazine sulphate, which is conveniently prepared by heating a benzene solution of benzylideneazine with methyl sulphate for five hours and decomposing the additive product with water, is exactly neutralised by sodium hydroxide, and the solution is treated with three times the calculated amount of 5*N*-nitrite and is made distinctly acid with acetic acid; when the mixture becomes neutral, acetic acid is again added, and so on for about eight hours until the methylhydrazine has been converted into *nitrosomethylhydrazine*, $NO\cdot NMe\cdot NH_2$, m. p. 45°, which is then liberated by sodium carbonate and extracted with ether. Its aqueous solution develops an intense violet coloration with ferric chloride, yields a white precipitate with

mercuric salts, and gives a reddish-brown, crystalline precipitate, and ultimately a reddish-brown coloration, with copper sulphate after the addition of sodium acetate or hydroxide. It reacts with an aqueous suspension of benzaldehyde containing a trace of sulphuric acid to form *nitrosobenzylidenemethylhydrazine*, CHPh:N·NMe·NO, m. p. 77—78°, with 10% sodium hydroxide and benzoyl chloride to form *benzoylnitrosomethylhydrazine*, NHBz·NMe·NO, m. p. 126—127° (decomp., rapidly heated), and with *N*/2-sodium hydroxide and benzenesulphonyl chloride to form *benzenesulphonylnitrosomethylhydrazine*, SO_2Ph·NH·NMe·NO, m. p. 83°; the last two compounds, like the corresponding *derivatives* of nitrosobenzylhydrazine,

NHBz·N(NO)·CH_2Ph,

m. p. 126—127°, and SO_2Ph·NH·N(NO)·CH_2Ph, m. p. 115—116°, do not develop a violet coloration with ferric chloride.

In methylhydrazine the nitrogen atom which is already alkylated is alone attacked by further methylation. Nitrosomethylhydrazine and nitrosobenzylhydrazine, however, readily react with methyl sulphate or benzyl chloride in the presence of aqueous sodium hydroxide, yielding *nitrosohydrazomethane*, NHMe·NMe·NO, b. p. 56°/10 mm., *nitroso-αβ-dibenzylhydrazine*, CH_2Ph·NH·N(NO)·CH_2Ph, m. p. 69°, *α-nitroso-β-benzyl-α-methylhydrazine*, CH_2Ph·NH·NMe·NO, m. p. 53°, and *α-nitroso-α-benzyl-β-methylhydrazine*, NHMe·N(NO)·CH_2Ph, m. p. 39°, all of which give intense blue colorations with ferric chloride instead of the violet colorations obtained with monoalkylated nitrosohydrazines. Since the group ·N:N·OH cannot be present in these four dialkylated nitrosohydrazines, it follows that this group is also not present in monoalkylated nitrosohydrazines, which therefore cannot have the symmetrical structure NHR·NH·NO, in which alone tautomerisation could occur in such a way as to form the group ·N:N·OH. α-Nitroso-β-benzyl-α-methylhydrazine and α-nitroso-α-benzyl-β-methylhydrazine exhibit very similar properties, but they depress each other's m. p., and the latter is changed into the former by mineral acids; the two substances are not identical, and consequently nitrosodialkylhydrazines cannot have the constitution $OH\cdot N{<}{\overset{NR}{\underset{NR'}{|}}}$.

Fission into an amine and nitrogen monoxide has been accomplished hitherto only in nitrosohydrazines of the aromatic series. Now it is shown that members of the aliphatic series decompose in a similar manner, by heating nitrosobenzylhydrazine with ethyl oxalate; the resulting amine is isolated partly as *benzyloxamide*, NH_2·CO·CO·NH·C_7H_7, m. p. 223°, mainly as *ethyl benzyloxamate*, CO_2Et·CO·NH·C_7H_7, m. p. 48°.

Sodium methylisoazoxide, NMe:N·ONa, is obtained in slender, white needles by treating methyl-alcoholic nitrosomethylhydrazine with sodium methoxide, ether, and ethyl nitrite; it inflames when heated or when treated with concentrated sulphuric acid, explodes in moist carbon dioxide, yields diazomethane when heated at 130—200°/12 mm., gives in aqueous or alcoholic solution a characteristic reddish-violet coloration with copper acetate, is reduced to methylhydrazine by 8—10% sodium hydroxide and aluminium, and is oxidised to methylnitroamine

by alkaline potassium ferricyanide. The *iso*diazomethane liberated from the sodium salt changes at once to diazomethane; thus, ordinary acids cause an evolution of nitrogen, benzoic acid produces methyl benzoate, hydrogen cyanide produces methylcarbylamine, and β-naphthol produces β-naphthyl methyl ether. Sodium benzyl*iso*azoxide (*loc. cit.*) is unstable, decomposes in carbon dioxide, yields benzyl alcohol with dilute sulphuric acid, and benzyl β-naphthyl ether with β-naphthol, is reduced to benzylhydrazine by aluminium and 8% sodium hydroxide, and is oxidised by alkaline potassium ferricyanide to *benzylnitroamine*, $CH_2Ph\cdot NH\cdot NO_2$, m. p. 38—39°, which forms a mercury *derivative*, $Hg(C_7H_7O_2N_2)_2$.

s-Dibenzylhydrazine is best prepared by the cathodic reduction of a methyl-alcoholic solution of benzylideneazine containing potassium hydroxide; its dinitroso-derivative has m. p. 44°, and yields *s*-diphenylazomethane when gently warmed in the absence of air. s-*Benzylmethylhydrazine dihydrochloride*, $NHMe\cdot NH\cdot CH_2Ph,2HCl$, m. p. 140° (decomp.), is obtained by boiling either of the nitrosobenzylmethylhydrazines with concentrated hydrochloric acid.

s-*Diphenylazomethane* (ω-*azotoluene*), $CH_2Ph\cdot N{:}N\cdot CH_2Ph$, m. p. 31·5°, is obtained by oxidising *s*-dibenzylhydrazine by 3% hydrogen peroxide and 20% ammonium hydroxide; it crystallises in colourless leaflets, and in alcoholic solution is converted into benzylidenebenzylhydrazone by a few drops of hydrochloric acid. In a similar manner, *s*-phenylbenzylhydrazine is oxidised to *benzeneazophenylmethane*, $NPh{:}N\cdot CH_2Ph$, an orange-coloured oil which readily changes to benzaldehydephenylhydrazone, slowly at the ordinary temperature, rapidly at 200°. C. S.

Formation of Hydrazones. UGO GRASSI (*Gazzetta*, 1910, **40**, ii, 139—153).—The formation of menthonephenylhydrazone from menthone and phenylhydrazine in ethyl-alcoholic solution is complete; it is unimolecular, and the velocity is proportional to the quantity of acid present. In methyl alcohol the velocity is less. The formation of camphorphenylhydrazone could not be followed by the polarimetric method employed for the menthone derivative, but it was found possible to obtain indications that the reaction proceeds three hundred times more slowly than in the case of the latter, when the concentration of acid is the same.

A formula is worked out for the determination of reaction constants based on the measurement of the partition of the phenylhydrazine between two ketones, of which one is optically active. In the case of methyl propyl ketone, methyl *iso*propyl ketone, and pinacolin, compared in this way with menthone, the following relative reaction constants (K_2/K_1) were found respectively: 5·3, 2·71, 1·29. It follows that the branching of the carbon chain diminishes the readiness of formation of hydrazones.

The author has devised another method founded on the fact that the conductivity of an alcoholic solution of phenylhydrazine and an acid diminishes when phenylhydrazine is withdrawn from the liquid, so that from conductivity measurements it is possible to calculate the quantity of phenylhydrazine remaining in the solution at any time. The solu-

tions employed were $0{\cdot}022N$ as regards the phenylhydrazine and the ketones, with $0{\cdot}0065N$-salicylic acid, and the observed conductivity ranged from 393 (initial) to 43 (final). The following are the reaction constants for the formation of phenylhydrazones of various ketones, the reactions being in all cases complete and unimolecular in the earlier stages: acetone, 0·122; methyl propyl ketone, 0·0228; methyl *iso*propyl ketone, 0·0114; pinacolin, 0·0043; benzaldehyde, 0·35; salicylaldehyde, 0·416; *m*-hydroxybenzaldehyde, 0·194; *p*-hydroxybenzaldehyde, 0·025; anisaldehyde, 0·061; protocatechualdehyde, 0·019; protocatechualdehyde carbonate, 0·123; piperonaldehyde, 0·048; vanillin, 0·060; *iso*vanillin, 0·048. Owing to the rapidity of the reactions, it was necessary to carry out the measurements at 10°. A simple thermostat is described convenient for this purpose, the low temperature being maintained by a supply of ice-water controlled by an electric thermoregulator. R. V. S.

Derivatives of α-Amino-*n*-butyric Acid. ARNOLD HILDESHEIMER (*Ber.*, 1910, **43**, 2796—2805).—*α-Phthalimino*-n-*butyric acid*,

$$C_8H_4O_2{:}N{\cdot}CHEt{\cdot}CO_2H,$$

is readily formed when the corresponding ester (Gabriel and Colman, Abstr., 1900, i, 359) is warmed with concentrated sulphuric acid for some three-quarters of an hour, and the mixture poured on to ice. It forms a resinous mass, which can be obtained in a crystalline form only with great difficulty, and then has m. p. 94—95°. The acid reacts with phosphorus pentachloride, yielding the corresponding acid chloride, which condenses with benzene in the presence of aluminium chloride, forming *phenyl phthaliminopropyl ketone*,

$$C_8H_4O_2{:}N{\cdot}CHEt{\cdot}COPh.$$

The ketone crystallises from light petroleum in colourless, six-sided plates, m. p. 118°, and on hydrolysis with hydrochloric acid yields *phenyl α-aminopropyl ketone hydrochloride*, $NH_2{\cdot}CHEt{\cdot}COPh,HCl$, m. p. 178° after sintering at 170°. The *picrate* has m. p. 174° after sintering at 160°, and the *platinichloride* has m. p. 190—200° (decomp.).

3 : 6-*Diphenyl*-2 : 5-*diethyl*-2 : 5-*dihydropyrazine*,

$$CPh{<}\begin{matrix}N{\cdot}CHEt\\CHEt{\cdot}N\end{matrix}{>}CPh,$$

is formed when an aqueous solution of phenyl aminopropyl ketone hydrochloride is mixed with ammonium hydroxide solution, the flask completely filled with air-free water, corked, and kept overnight. The *hydrochloride*, $C_{20}H_{23}N_2Cl$, forms a red, crystalline mass, m. p. 167—168° (decomp.).

The base and its hydrochloride are readily oxidised, even on exposure to the air; with dilute nitric acid, oxidation is instantaneous, and the product is Collet's 3 : 6-diphenyl-2 : 5-diethylpyrazine. On hydrolysis with hydrochloric acid in an atmosphere of carbon dioxide, the dihydro-base yields mainly phenyl α-aminopropyl ketone, with probably a small amount of the isomeric ketone, $NH_2{\cdot}CHPh{\cdot}COEt$ (compare Gabriel, Abstr., 1908, i, 466).

Potassium thiocyanate reacts with an aqueous solution of phenyl aminopropyl ketone hydrochloride, yielding 2-*thiol*-5(or 4)-*phenyl*-4

(or 5)-*ethylglyoxaline*, $\begin{matrix}CPh\cdot NH\\ \|\\ CEt—N\end{matrix}\!\!>\!C\cdot SH$ or $\begin{matrix}CPh—N\\ \|\\ CEt\cdot NH\end{matrix}\!\!>\!C\cdot SH$, in the form of snow-white needles, m. p. 272° after changing colour at 260°. Nitric acid oxidises the thiol to $\alpha\beta$-phenylethylthiazole, $C_{11}H_{12}N_2$, m. p. 172°.

α-Phthaliminobutyric acid reacts with red phosphorus and bromine (compare Gabriel, Abstr., 1908, i, 182), yielding *$\alpha\beta$-dibromo-α-phthaliminopropane*, $C_8H_8O_2{:}N\cdot CHBr\cdot CHMeBr$, which crystallises from alcohol in well-developed octahedra, m. p. 147°. When boiled for an hour with water, the bromo-derivative yields phthalimide, hydrogen bromide (1 mol.), and α-bromopropaldehyde according to the equation: $C_8H_4O_2{:}N\cdot CHBr\cdot CHBrMe + H_2O = C_8H_4O_2 + HBr + CHMeBr\cdot CHO$. The α-bromopropaldehyde was identified by treatment with sodium acetate and then with phenylhydrazine, when Pinkus' acetolphenylhydrazone (Abstr., 1898, i, 224) was obtained. Hydroxyacetone can be prepared from aminoacetone hydrochloride by the action of nitrous acid, and Nef has shown that it is readily formed from α-hydroxypropaldehyde. J. J. S.

Furoylacetic Ester and the Furylpyrazolones. III. HENRY A. TORREY and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1910, **44**, 5, 391—431. Compare Abstr., 1907, i, 146; 1908, i, 840).—The authors have studied the influence of the furyl group in ethyl furoylacetate and its pyrazolone derivatives, and have synthesised a new analogue of antipyrine containing the furyl group.

An improved method for preparing ethyl furoylacetate is described; the *sodium* and *potassium* salts were prepared; the *oxime*,

$$C_4OH_3\cdot C(NOH)\cdot CH_2\cdot CO_2Et,$$

crystallises in long, white, silky needles, m. p. 131—132°. When hydroxylamine acts on ethyl furoylacetate in the presence of potassium hydroxide, *3-furylisooxazolone*, $O\!<\!\begin{matrix}N{=}C\cdot C_4OH_3\\ |\\ CO\cdot CH_2\end{matrix}$, is obtained, crystallising in long, flat needles, m. p. 148—149°.

Ethyl furoylacetate forms a *semicarbazone*, which crystallises in small, flat, rhombic plates, and an *oximino*-derivative,

$$C_4OH_3\cdot CO\cdot C({:}NOH)\cdot CO_2Et,$$

m. p. 128—129°. By the action of phenylcarbimide, *ethyl furoylmalonanilate*, $C_4OH_3\cdot CO\cdot CH(CO\cdot NHPh)\cdot CO_2Et$, is produced, crystallising in white needles, m. p. 146—150°.

3-Furyl-5-pyrazolone, $C_4OH_3\cdot C\!<\!\begin{matrix}N—NH\\ |\\ CH_2\cdot CO\end{matrix}$, crystallises in small, rectangular plates, m. p. 223° (decomp.); its *picrate* decomposes at 192°. By the action of acetic anhydride on the pyrazolone, *1-acetyl-3-furyl-5-pyrazolone*, m. p. 153—154°, is obtained; the corresponding 1:2-*diacetyl* derivative forms long, silky needles, m. p. 102°. *Phenylcarbamyl furylpyrazolone*, $\begin{matrix}C_4OH_3\cdot C{=}N\\ |\\ CH_2\cdot CO\end{matrix}\!\!>\!N\cdot CO\cdot NHPh$, m. p. 192°, is obtained by the action of phenylcarbimide on the pyrazolone, and *4-benzylidene-3-furyl-5-pyrazolone*, $\begin{matrix}C(C_4OH_3){=}N\\ |\\ C({:}CHPh)\cdot CO\end{matrix}\!\!>\!NH$, by the

action of benzaldehyde. The azo-derivative, 4-*benzeneazo*-3-*furyl*-5-*pyrazolone*, crystallises in red, transparent prisms, m. p. 182—183°.

1-*Phenyl*-3-*furyl*-5-*pyrazolone hydrochloride*, $C_{13}H_{10}O_2N_2,HCl$, crystallises in small, white needles, m. p. 122—123°. By the action of acetic anhydride on 1-phenyl-3-furyl-5-pyrazolone, 2-*acetyl*-1-*phenyl*-3-*furyl*-5-iso*pyrazolone*, $\begin{matrix} C_4H_3O\cdot C\cdot NAc \\ \parallel \quad\quad \\ CH\cdot CO \end{matrix}\!\!>\!NPh$, m. p. 69—72°, is obtained in small, flat, slightly yellow prisms. 5-*Benzoyloxy*-1-*phenyl*-3-*furylpyrazole*, $C_4OH_3\cdot C\!\!<\!\!\begin{matrix} N—NPh \\ CH:C\cdot OBz \end{matrix}$, melts at 113—114°, and 4-*oximino*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix} C_4OH_3\cdot C{=}N \\ OH\cdot N:C\cdot CO \end{matrix}\!\!>\!NPh$, decomposes at 183—184°. By the action of benzaldehyde on the pyrazolone, 4-*benzylidene*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, decomposing at 210—212°, is obtained. 4-*Benzeneazo*-1-*phenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix} C_4OH_3\cdot C{=\!=}N \\ N_2Ph\cdot CH—CO \end{matrix}\!\!>\!NPh$, crystallises in long, light red needles, m. p. 165°. 4-β-*Naphthaleneazo*-1-*phenyl*-3-*furyl*-5-*pyrazolone* crystallises in deep, red needles, m. p. 202—203°. The *hydriodide*, m. p. 192—193°; the *hydrochloride*, m. p. 197—198°; the *hydrobromide*, m. p. 194°, and the *picrate*, m. p. 157—158°, of 1-phenyl-3-furyl-2-methyl-5-pyrazolone are described. 4-*Nitroso*-1-*phenyl*-3-*furyl*-2-*methyl*-5-iso*pyrazolone*,

$$\begin{matrix} C_4H_3O\cdot C\cdot NMe \\ \parallel \quad\quad \\ NO\cdot C—CO \end{matrix}\!\!>\!NPh,$$

crystallises in green needles, m. p. 185°; its *hydrochloride* crystallises in bright red needles, decomposing at 189°.

1-p-*Bromophenyl*-3-*furyl*-5-*pyrazolone*, $\begin{matrix} C_4OH_3\cdot C{=\!=}N \\ CH_2\cdot CO \end{matrix}\!\!>\!N\cdot C_6H_4Br$, prepared from *p*-bromophenylhydrazine and ethyl furoylacetate, crystallises in needles, m. p. 160—161°.

3-*Furyl*-5-*pyrazolone*-1-*benzene*-p-*sulphonic acid* crystallises in small plates, turning brown when kept. 1-m-*Nitrophenyl*-3-*furyl*-5-*pyrazolone* crystallises in yellowish-brown prisms, m. p. 174—175°.

2-*Phenyl*-3-*furyl*-4-iso*pyrazolone*, $\begin{matrix} C_4OH_3\cdot C\cdot NPh \\ \parallel \quad\quad \\ CH\cdot CO \end{matrix}\!\!>\!NH$, crystallises in transparent prisms, m. p. 176°. N. C.

Quinazolines. XXV. Synthesis of 6- and 7-Amino-2-methyl-4-quinazolones from 4- and 5-Acetylaminoacetylanthranils. MARSTON T. BOGERT, CARL GUSTAVE AMEND, and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1910, **32**, 1297—1312).—4- and 5-Acetylaminoacetylanthranils have been prepared by acetylating the corresponding tolylenediamines, oxidising the acetyl derivatives with a neutral solution of potassium permanganate, and treating the resulting diacetylaminobenzoic acids with excess of acetic anhydride. The oxidation of 2 : 5-diacetylaminotoluene proved much more difficult than that of the 2 : 4 compound, and gave a much smaller yield of the diacetylaminobenzoic acid.

When these acetylaminoacetylanthranils are condensed with primary

amines, acetylamino-4-quinazolones are produced, and, on eliminating the acetyl group, the 6- or 7-amino-2-methylquinazolones are obtained. Nearly all the quinazolones now described are crystalline solids of high m. p. or b. p.

4-*Acetylaminoacetylanthranil*, $\mathrm{NHAc\cdot C_6H_3<}\begin{array}{l}\mathrm{CO}\\ \mathrm{NAc}\end{array}$, m. p. 220° (corr.), crystallises in colourless needles. 2 : 5-*Diacetylaminobenzoic acid*, $C_6H_3(NHAc)_2\cdot CO_2H$, m. p. 262° (decomp., corr.), forms minute, colourless crystals. 5-*Acetylaminoacetylanthranil*, m. p. 253° (corr.), crystallises in needles. The 4- and 5-acetylaminoacetylanthranils absorb moisture, and are re-converted into the corresponding diacetylaminobenzoic acids.

The following quinazolones were prepared from 4-acetylaminoacetylanthranil. 7-*Acetylamino-2-methyl-4-quinazolone* (4-*hydroxy-7-acetylamino-2-methylquinazoline*),

$$\mathrm{NHAc\cdot C_6H_3<}\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CO{-}NH}\end{array} \rightleftarrows \mathrm{NHAc\cdot C_6H_3<}\begin{array}{l}\mathrm{N{=\!=}CMe}\\ \mathrm{C(OH){:}N}\end{array},$$

m. p. 344° (corr.), crystallises in slender, silky needles, containing $2H_2O$, and when boiled with dilute potassium hydroxide is converted into 7-amino-2-methyl-4-quinazolone (Bogert and Klaber, Abstr., 1908, i, 466). The latter compound does not react with phenylhydrazine or ethyl chloroacetate; when boiled with formaldehyde and potassium cyanide, a reaction takes place, but the product does not contain any new substances; its *potassium* salt, *hydrochloride*, and *platinichloride* are described.

Dinitro-7-acetylamino-2-methyl-4-quinazolone, m. p. 302° (decomp.), forms orange crystals; the nitro-groups probably occupy the 6- and 8-positions. *Bromo-7-acetylamino-2-methyl-4-quinazolone*, m. p. 292° (corr.), crystallises in minute needles, and, when boiled with 10% potassium hydroxide solution, is converted into *bromo-7-amino-2-methyl-4-quinazolone*, m. p. 272—273° (corr.), which forms light yellow, flaky crystals. 7-*Formylamino-2-methyl-4-quinazolone*, m. p. 339—340° (corr.), forms colourless, feathery crystals, and the corresponding *propionyl* derivative, m. p. 326—327° (corr.), crystallises in long, white, silky needles. When a solution of 7-amino-2-methyl-4-quinazolone in dilute hydrochloric acid is treated with sodium nitrite at 0° and the product boiled and afterwards neutralised with sodium carbonate, 7-*hydroxy-2-methyl-4-quinazolone*, $\mathrm{OH\cdot C_6H_3<}\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CO\cdot NH}\end{array}$, is obtained as a light brown powder, which darkens at about 345°, but does not melt at this temperature; its *acetyl* derivative, m. p. 266° (corr.), forms large, pale brown needles. If the diazotisation product of 7-amino-2-methyl-4-quinazolone is boiled with a solution of copper potassium cyanide, 7-*cyano-2-methyl-4-quinazolone*, $\mathrm{CN\cdot C_6H_3<}\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CO\cdot NH}\end{array}$, m. p. 303—304° (corr.), is produced, which crystallises in colourless, feathery needles.

7-*Acetylamino-2 : 3-dimethyl-4-quinazolone*, $\mathrm{NHAc\cdot C_6H_3<}\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CO\cdot NMe}\end{array}$,

m. p. 284° (corr.), obtained by the action of methylamine on 4-acetylaminoacetylanthranil, forms colourless, silky needles. 7-*Amino*-2 : 3-*dimethyl*-4-*quinazolone*, m. p. 224° (corr.), crystallises in needles or prisms; its *platinichloride* is described. 7-*Acetylamino*-2-*methyl*-3-*ethyl*-4-*quinazolone*, m. p. 254° (corr.), forms short, colourless needles or lustrous plates. 7-*Acetylamino*-2-*methyl*-3-n-*propyl*-4-*quinazolone*, m. p. 206—207° (corr.), crystallises in rosettes of needles. 4-Acetylaminoacetylanthranil does not undergo condensation with *sec.*-butylamine, but yields 2 : 4-*diacetylaminobenzo*-sec.-*butylamide*,

$$C_6H_3(NHAc)_2\cdot CO\cdot NH\cdot C_4H_9,$$

m. p. 235° (corr.), which forms colourless needles. 7-*Acetylamino*-2-*methyl*-3-iso*amyl*-4-*quinazolone* has m. p. 288° (corr.), and the corresponding 3-*phenyl*, 3-p-*anisyl*, 3-p-*phenetyl*, and 3-α-*naphthyl* derivatives have m. p. 276°, 273°, 259°, and 256° (corr.) respectively. When 4-acetylaminoacetylanthranil is heated with *p*-aminobenzonitrile, a quinazolone is not produced, but a *compound*, m. p. 258° (corr.), is obtained, containing 12·4% of nitrogen.

When hydrazine hydrate (1 mol.) is boiled with 4-acetylaminoacetylanthranil (1 mol.), 3-*amino*-7-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 268° (corr.), is produced, which crystallises with $1H_2O$, and fails to give the Bülow condensation (Abstr., 1906, i, 906, 981) with ethyl diacetylsuccinate; the *hydrochloride* has m. p. 312° (decomp.). If 4-acetylaminoacetylanthranil is treated in the cold with 50% hydrazine hydrate solution, 2 : 4-*diacetylaminobenzoylhydrazide*,

$$C_6H_3(NHAc)_2\cdot CO\cdot NH\cdot NH_2,$$

is produced, which crystallises in short, slender needles, and melts at 268° with formation of 7-acetylamino-3-amino-2-methyl-4-quinazolone. 3 : 7-*Diacetylamino*-2-*methyl*-4-*quinazolone*, m. p. 304° (corr.), forms minute, colourless crystals, and, when boiled with dilute potassium hydroxide, is converted into 3 : 7-*diamino*-2-*methyl*-4-*quinazolone*, m. p. 238° (corr.), which forms silky needles.

3-*Anilino*-7-*acetylamino*-2-*methyl*-4-*quinazolone*,

$$NHAc\cdot C_6H_3{<}\begin{matrix}N{=}CMe\\ \quad\ \ |\\ CO\cdot N(NHPh)\end{matrix},$$

m. p. 214° (corr.), obtained by the action of phenylhydrazine on 4-acetylaminoacetylanthranil, forms colourless, feathery needles.

7-*Acetylamino*-2-*methyl*-4-*quinazolonyl*-3 : 7′-(2′-*methyl*-4′-*quinazolone*),

$$NHAc\cdot C_6H_3{<}\begin{matrix}N{=}CMe\\ \quad\ |\\ CO{-}N\cdot C_6H_3{<}\begin{matrix}N{=}CMe\\ \quad |\\ CO\cdot NH\end{matrix}\end{matrix},$$

m. p. 335° (corr.), obtained by the condensation of 7-amino-2-methyl-4-quinazolone with 4-acetylaminoacetylanthranil, crystallises in short, stout, pale yellow needles.

The following quinazolones were prepared from 5-acetylaminoacetylanthranil. 6-*Acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 350° (corr.), forms colourless needles or prisms. 6-*Amino*-2-*methyl*-4-*quinazolone*, m. p. 314—315° (corr.), crystallises in rosettes of needles. 6-*Acetylamino*-2 : 3-*dimethyl*-4-*quinazolone*, m. p. 278° (corr.), and 6-*acetylamino*-2-*methyl*-3-*ethyl*-4-*quinazolone*, m. p. 229° (corr.), form colourless, silky needles. The corresponding 3-n-*propyl* and 3-*phenyl*

derivatives have m. p. 181° and 255° (corr.) respectively. 3-*Amino*-6-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 262—263° (corr.), obtained by heating 5-acetylaminoacetylanthranil with dilute hydrazine hydrate, crystallises in rosettes of colourless, silky needles. E. G.

Diguanide and Compounds Derived from It. KAROL RACKMANN (*Annalen*, 1910, **376**, 163—183. Compare Bamberger and Dieckmann, Abstr., 1892, 737; Söll and Stutzer, this vol., i, 14).—Diguanide has been prepared by a modification of Herth's method (Abstr., 1881, 896), using soda-water bottles in place of sealed tubes. The sulphate can be obtained from the copper derivative by treatment with 10% sulphuric acid, and the free base from the sulphate by the action of barium hydroxide. Diguanide, $NH[C(NH_2):NH]_2$, crystallises from absolute alcohol in glistening prisms, m. p. 130°, and its aqueous solution decomposes gradually when kept. The *carbonate*, $C_2H_5N_7,H_2CO_3$, crystallises in prisms, sparingly soluble in alcohol; the normal *hydrochloride*, $C_2H_5N_7,HCl$, forms glistening needles, m. p. 235°, and the acid *hydrochloride*, $C_2H_5N_7.2HCl$, large plates, m. p. 248°. The *nitrate*, $C_2H_5N_7,HNO_3$, crystallises in large, glistening prisms, m. p. 192°; the *acetate*, $C_2H_5N_7,CH_3\cdot CO_2H$, has m. p. 268°, the *oxalate*, $C_2H_5N_7,C_2O_4H_2$, m. p. 210°, and the *chloroacetate*, m. p. 186°. The *cyanoacetate* forms soluble, glistening plates, and the *succinate*, $2C_2H_5N_7,C_2H_4(CO_2H)_2$, colourless crystals.

Oxalyldiguanide, $\begin{matrix}CO\cdot NH\cdot C(:NH)\\ |\\ CO\cdot NH\cdot C(:NH)\end{matrix}\!\!>\!NH$, prepared by the action of ethyl oxalate on diguanide, crystallises from alcohol in large, colourless needles, which decompose above 300°. It does not react with ethyl oxalate or ethyl malonate, but when warmed with dilute hydrochloric acid yields *diguanidino-oxalic acid*,

$$CO_2H\cdot CO\cdot NH\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH_2,$$

which crystallises in long, thin needles, m. p. 240°. The *sodium* salt, $C_4H_6O_3N_5Na$, forms long needles, and the *barium* salt, small, sparingly soluble needles.

Malonyldiguanide (4 : 6-*diketo*-2-*guanidinopyrimidine*),

$$NH:C(NH_2)\cdot NH\cdot C{<}\begin{matrix}NH\cdot CO\\ N-CO\end{matrix}{>}CH_2,$$

prepared by boiling an alcoholic solution of diguanide with ethyl malonate, crystallises in small needles, and has not acidic properties. The *hydrochloride*, $C_5H_7O_2N_5,HCl$, forms feathery needles, and the *sulphate*, $2C_5H_7O_2N_5,H_2SO_4$, large needles. *Succinyldiguanide*,

$$NH:C(NH_2)\cdot NH\cdot C{<}\begin{matrix}NH\cdot CO\cdot CH_2\\ \quad\quad\quad\ \ |\\ N-CO-CH_2\end{matrix},$$

is only formed in the absence of all traces of water, and has feebly basic properties. The *sulphate*, $C_6H_9O_2N_5,H_2SO_4$, crystallises in large needles, the *hydrochloride*, $C_6H_9O_2N_5,2HCl$, in slender needles, and the *picrate*, $C_6H_9O_2N_5,C_6H_3O_7N_3$, in brilliant, large needles, m. p. 220°.

A theoretical yield of ammeline can be obtained by condensing diguanide with an absolute alcoholic solution of ethyl carbonate, and a theoretical yield of thioammeline by condensing diguanide with an alcoholic solution of hydrogen sulphide. The symmetrical constitu-

tional formulæ for these two compounds are regarded as established beyond dispute by these syntheses, and also the symmetrical formulæ of other cyanuric acid derivatives.

When diguanide is condensed in aqueous solution with carbon disulphide, the *product* consists of somewhat unstable, reddish-brown crystals, $C_3H_5N_5S_2$.

Formylguanamine (1:3-diamino-1:3:5-triazine) (Bamberger and Dieckmann: Abstr., 1892, *loc. cit.*) can be synthesised from diguanide and ethyl formate in absolute alcoholic solution.

Phenylguanamine (3:5-*diamino*-1-*phenyl*-1:3:5-*triazine*),

$$N{<}{\begin{matrix}C(NH_2)\cdot N\\ C(NH_2){:}N\end{matrix}}{>}CPh,$$

prepared by the action of benzoyl chloride and alkali on diguanide sulphate, crystallises from water in large prisms, m. p. 222°, and yields a *picrate*, m. p. 228°.

Diguanide reacts with an alcoholic solution of chloroacetic acid, yielding *diguanidinoacetic acid*, $C_2H_6N_5\cdot CH_2\cdot CO_2H$, in the form of its hydrochloride. The acid crystallises from aqueous alcohol in long needles, and reacts with both acids and alkalis. The *sodium* salt, $C_4H_8O_2N_5Na$; *hydrochloride*, $C_4H_9O_2N_5,HCl$, and *picrate*,

$$C_4H_9O_2N_5,C_6H_3O_7N_3,$$

m. p. 202°, are described. J. J. S

Synthesis of Tetrazoles from Arylazoimides. OTTO DIMROTH and SIEGFRIED MERZBACHER (*Ber.*, 1910, **43**, 2899—2904. Compare Abstr., 1907, i, 659).—Extending to acetaldehydephenylhydrazone and glyoxylic acid phenylhydrazone the reaction with phenylazoimide previously studied, the authors have been able to isolate *N*-benzeneazoacetophenylhydrazidine, $NHPh\cdot N{:}N\cdot CMe{:}N\cdot NHPh$ or

$$NPh{:}N\cdot NH\cdot CMe{:}N\cdot NHPh,$$

and *N*-benzeneazo-oxalophenylhydrazidine,

$$NHPh\cdot N{:}N\cdot C(CO_2H){:}N\cdot NHPh,$$

as intermediate products. The former substance when treated with hydrochloric acid yields benzenediazonium chloride and acetophenylhydrazidine, $CMe(NH_2){:}N\cdot NHPh$. The second product cannot be decomposed in that way, but benzeneazo-5-hydroxy-1-phenyl-1:2:3-triazole (compare Dimroth and Eberhardt, Abstr., 1905, i, 99) is formed when its sodium salt is treated with benzoyl chloride and sodium hydroxide. These hydrazidine derivatives could not be converted into tetrazoles. When, however, tribromophenylazoimide reacts with the hydrazones mentioned, the intermediate products are labile; they lose tribromoaniline spontaneously, 1-phenyl-4-methyl-1:2:3:5-tetrazole and 1-phenyl-1:2:3:5-tetrazole-4 carboxylic acid being obtained.

N-*Benzeneazoacetophenylhydrazidine*, obtained by heating acetaldehydephenylhydrazone and phenylazoimide in alcoholic sodium ethoxide solution for forty hours on the water-bath, crystallises in reddish-yellow, rhomboidal tablets, m. p. 101° (with evolution of gas). In contact with dilute hydrochloric acid, it gradually dissolves with evolution of gas, and from the solution *acetophenylhydrazidine hydrochloride*, $C_8H_{12}N_3Cl,\frac{1}{2}H_2O$, can be obtained (compare

Voswinckel, Abstr., 1902, i, 844). It melts at 140°, resolidifies, and melts again (not sharply) at 205°.

The *sodium* salt of N-*benzeneazo-oxalomonophenylhydrazidine*,

$$C_{14}H_{12}O_2N_5Na,3H_2O,$$

is prepared by heating glyoxylic acid phenylhydrazone and phenylazoimide in alcoholic sodium ethoxide solution for fifteen minutes on the water-bath. It is a yellow, crystalline substance, which becomes red in excess of sodium hydroxide in consequence of the formation of a disodium salt. With acids, it yields the free *acid* as a flocculent precipitant, which soon decomposes with evolution of gas even in the cold.

1-*Phenyl*-4-*methyl*-1 : 2 : 3 : 5-*tetrazole*, PhN·N:N·CMe:N, is best freed from the accompanying tribromoaniline by extraction with ether and subsequent distillation in a vacuum, the distillate being collected at 140°/15 mm. It crystallises in long, flat, colourless needles, m. p. 40°, and has an odour of jasmine, although the isomeric 1-phenyl-5-methyl-1 : 2 : 3 : 4-tetrazole (following abstract) has no smell.

R. V. S.

Diazohydrazides. OTTO DIMROTH and GUILLAUME DE MONTMOLLIN (*Ber.*, 1910, **43**, 2904—2915. Compare preceding abstract).—The diazohydrazides from monoacylhydrazines condense to 1 : 2 : 3 : 4-tetrazoles when treated with alkalis, indicating that they are β-diazohydrazides of the type NAr:N·NH·NH·CO·R (compare Curtius, Abstr., 1893, i, 463). The diazo-derivatives of the diacylhydrazines also yield tetrazoles with alkalis, an acyl group being eliminated, and in many cases (for example, 5-hydroxy-1-phenyltetrazole) this synthesis offers the best means of preparing tetrazole derivatives. It was not found possible to prepare the bisdiazohydrazides,

NAr:N·NAc·NAc·N:NAr,

from which pentazoles might have been obtained by a method analogous to that described in the preceding abstract. Only monoacyldiazohydrazides can react with a second molecule of a diazonium salt, and they then undergo a tautomeric rearrangement, such that the reaction product spontaneously decomposes into the diazoamido-compound and the azoimide of the acid group.

Diacylhydrazines do not react with diazonium salts in acid solution. The diazohydrazides are readily obtained as white or yellow, usually flocculent, precipitates, however, when aqueous solutions of the diacylhydrazides are treated with a slight excess of sodium carbonate, and then with the equivalent quantity of the neutralised diazonium chloride solution. The temperature is maintained at −10°, salt being added to prevent freezing. On addition of sodium hydroxide, the precipitate is converted into the tetrazole derivative. 1-Phenyl-1 : 2 : 3 : 4-tetrazole was obtained by the use of diformylhydrazine (the diazohydrazide from which is very unstable), and it has the properties formerly described. 1-p-*Tolyl*-1 : 2 : 3 : 4-*tetrazole*, $C_8H_8N_4$, forms colourless needles, m. p. 96°. 1-*p*-Nitrophenyltetrazole may be obtained similarly.

1-*Phenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, NPh·N:N·N:CMe (from

diacetylhydrazine), forms lanceolate crystals, m. p. 97·5°. p-*Toluene-azodiacetylhydrazine*, $C_7H_7N_2\cdot NAc\cdot NHAc$, is more stable than the phenyl derivative. It forms small, pale brown crystals, m. p. 60° (decomp.). 1-p-*Tolyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, $C_9H_{10}N_4$, has m. p. 106°. p-*Nitrobenzeneazodiacetylhydrazine*, $C_{10}H_{11}O_4N_5$, forms colourless, lustrous crystals, m. p. 107° (with evolution of gas). It can be preserved unchanged in the dry state for months. 1-p-*Nitrophenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazole*, $C_8H_7O_2N_5$, crystallises in pale yellow plates, m. p. 129°.

The diazohydrazides from dibenzoylhydrazine are more unstable than those from diacetylhydrazine. It is necessary to dissolve the hydrazine in dilute sodium hydroxide, owing to its slight solubility in water. *Benzeneazodibenzoylhydrazine* was obtained as a white, unstable precipitate.

5-Hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrazole, obtained from ethyl hydrazinedicarboxylate and benzenediazonium chloride, is identical with the phenylhydroxytetrazole of Freund and Hempel (Abstr., 1895, i, 193).

Tribromobenzenediazonium salts react (but incompletely) with ethyl hydrazinedicarboxylate in weakly acid solution. *Ethyl tribromobenzeneazohydrazinedicarboxylate*, $C_6H_2Br_3N_2\cdot N(CO_2Et)\cdot NH\cdot CO_2Et$, is better obtained in presence of sodium carbonate. It forms small, colourless needles, which explode at 111—115°, according to the rate of heating. The compound can be preserved unchanged. Ethereal hydrogen chloride decomposes it into its components. It was not possible to prepare the corresponding tetrazole.

The monoacylhydrazines react with diazonium salts, not only in alkaline, but also in acid solution. Most of the diazohydrazides are too unstable to be isolated and purified. *Benzeneazoacethydrazide* and p-*tolueneazoacethydrazide* are white precipitates, which are rapidly converted into the tetrazoles when treated with sodium hydroxide. p-*Nitrobenzeneazoacethydrazide*, $NO_2\cdot C_6H_4\cdot N_2\cdot NH\cdot NHAc$, is soluble in dilute sodium hydroxide with production of an intense, bluish-red coloration, which afterwards disappears, and the tetrazole is formed. With *p*-toluenediazonium chloride in solution containing alkali hydroxide, it yields *p*-nitrobenzenediazoaminotoluene (Bamberger, Abstr., 1895, i, 351), a smell of *p*-tolylazoimide is observed, and azoimide is found in the filtrate. *Sulphobenzeneazoacethydrazide*, $SO_3H\cdot C_6H_4\cdot N_2\cdot NH\cdot NH\cdot Ac$, is obtained by the method described in the form of its *sodium* salt, which is very stable when dry. Water slowly effects an anomalous decomposition, azoimide and sodium sulphanilate being produced. The substance reacts with *p*-toluenediazonium chloride only in the presence of sodium hydroxide, azoimide and sodium *p*-toluenediazoaminobenzenesulphonate being formed. With sodium hydroxide the diazohydrazide yields the *sodium* salt of 1-*phenyl*-5-*methyl*-1 : 2 : 3 : 4-*tetrazolesulphonic acid*,

$$SO_3H\cdot C_6H_4\cdot \underline{N\cdot N{:}N\cdot N{:}C}Me,$$

in crystalline form. The *silver* salt, $C_8H_7O_3N_4SAg$, crystallises in flat, lustrous prisms.

Benzeneazobenzhydrazide (Curtius, *loc. cit.*) is converted by sodium

hydroxide into 1 : 5-diphenyl-1 : 2 : 3 : 4-tetrazole, identical with that of Schröter (Abstr., 1909, i, 617, 773).

5-*Phenyl*-1-p-*nitrophenyl*-1 : 2 : 3 : 4-*tetrazole*, $C_{13}H_9O_2N_5$, is produced, in addition to *p*-nitrophenylazoimide and a green *sodium* salt, when *p*-nitrobenzeneazobenzhydrazide (von Pechmann, Abstr., 1896, i, 678) is dissolved in sodium hydroxide. It forms yellow prisms, m. p. 149°. The nitrophenylphenyltetrazole, m. p. 177—178°, obtained by Schröter must therefore have the structure:

$$Ph\cdot\underline{N\cdot N:N\cdot N:C}\cdot C_6H_4\cdot NO_2.$$

Semicarbazide reacts with benzene- and with *p*-toluene-diazonium chlorides in acetic acid solution, yielding crystalline diazohydrazides. The *toluene* derivative is the more stable. It forms colourless laminæ, which decompose rapidly even when dry. An ethereal solution, when kept in the cold, deposits carbamoazoimide of m. p. 97°, and in the filtrate *p*-toluidine is present. Tolueneazosemicarbazide does not yield the corresponding tetrazole when treated with alkali. The action of a cold alcoholic solution of sodium ethoxide gives rise to sodium azoimide, diazoaminotoluene, *p*-toluidine, and sodium carbonate. Hence it is possible that in this diazohydrazide the azo-group is attached in the *a*-position. R. V. S.

Action of Diazo-compounds on Ethyl Glutaconate. FERDINAND HENRICH, W. REICHENBURG, G. NACHTIGALL, W. THOMAS, and C. BAUM (*Annalen*, 1910, 376, 121—151. Compare Abstr., 1899, i, 794; Dimroth and Hartmann, Abstr., 1909, i, 66).—The products obtained by the action of diazonium salts (1 mol.) on ethyl glutaconate are yellow, and have the constitution of azo-compounds, for example,

$$CO_2Et\cdot CH:CH\cdot CH(CO_2Et)\cdot N:NPh,$$

or the tautomeric hydrazone formula,

$$CO_2Et\cdot CH:CH\cdot C(CO_2Et):N\cdot NHPh.$$

The fact that they can be boiled with alcohol or even distilled without decomposition and that they do not couple with R-salt indicates that they cannot have the diazo-constitution $>C(OEt)\cdot O\cdot N_2R$ (compare Dimroth, *loc. cit.*), although it is highly probable that such diazo-compounds are formed as unstable intermediate products in the preparation of the stable azo-compounds.

The condensation takes place most readily in an aqueous alcoholic solution of the ester, and in the presence of sodium acetate and an aqueous solution of the diazonium salt. The reaction proceeds slowly, and is complete in half to one hour.

When an excess of diazonium salt is used, a compound of the type $CO_2Et\cdot C(N_2Ph):CH\cdot C(CO_2Et):N\cdot NHPh$ is formed. These compounds are quite different from the formazyl derivatives described previously, (Heinrich and Thomas, Abstr., 1908, i, 114); they have an intense red colour, and readily lose the elements of ethyl alcohol when heated with alcohol, yielding pyridazone derivatives:

$$CO_2Et\cdot C(:N\cdot NHR)\cdot CH:C(CO_2Et)\cdot N:NR \longrightarrow$$
$$EtOH + CH{<}{\begin{matrix}C(CO_2Et)=N\\C(N:NPh)\cdot CO\end{matrix}}{>}NR$$

This decomposition proceeds at very different rates with the different condensation products, those containing ortho-substituents in the benzene nuclei being most stable. When such substituents are present, the elimination of the alcohol is effected by heating with acetic anhydride, but in the case of the mesitylene derivative, even this reagent is without action. The stability of the compounds depends not merely on the positions of the substituents, but also on their chemical nature, the more electro-positive the ortho-substituent the greater its stabilising effect. The pyridazone derivatives are brown or brownish-yellow solids, the colour being palest when halogen substituents are present in *m*- or *p*-positions; they are stable towards dilute acids or aqueous solutions of alkalis, but dissolve in concentrated sulphuric acid, yielding reddish-yellow solutions.

Ethyl glutacononate phenylhydrazone,

$$CO_2Et\cdot CH\colon CH\cdot C(CO_2Et)\colon N\cdot NHPh$$

(or desmotropic formula), separates from alcohol in long, pale yellow, glistening crystals, m. p. 67—68°. *Ethyl* 3-*benzeneazoglutacononate phenylhydrazone*, $N_2Ph\cdot C(CO_2Et)\colon CH\cdot C(CO_2Et)\colon N\cdot NHPh$, separates from a boiling mixture of benzene and light petroleum (1 : 4) in brilliant, glistening, rhombic crystals [$a:b:c = 0\cdot4423:1:0\cdot6561$], m. p. 117° (decomp); it gives Bulow's reaction, and is decomposed to a certain extent when boiled for some time with benzene. *Ethyl* 5-*benzeneazo*-1-*phenyl*-6-*pyridazone*-3-*carboxylate*,

$$CH\Big\langle\begin{matrix}(CO_2Et)=N\\(N_2Ph)-CO\end{matrix}\Big\rangle NPh,$$

crystallises from alcohol in brownish-yellow needles, m. p. 161°.

Ethyl 3-o-*tolueneazoglutacononate* o-*tolylhydrazone*,

$$C_6H_4Me\cdot N\colon N\cdot C(CO_2Et)\colon CH\cdot C(CO_2Et)\colon N\cdot NH\cdot C_6H_4Me,$$

forms dark red, glistening crystals, m. p. 134°, after sintering at 130°, and the corresponding *ethyl* 5-o-*tolueneazo*-1-o-*tolyl*-6-*pyridazone*-3-*carboxylate*, $C_{21}H_{20}O_3N_4$, crystallises in dark brown needles, m. p. 152° after sintering at 150°; the isomeric 5-p-*tolueneazo*-1-p-*tolyl* compound forms pale brown-coloured needles, m. p. 157°, and is prepared readily from *ethyl* 3-p-*tolueneazoglutacononate* p-*tolylhydrazone*, $C_{23}H_{26}O_4N_4$, which resembles the ortho-compound, and has m. p. 124—125° after sintering at 120°.

Ethyl glutacononate as.-m-*xylylhydrazone*,

$$CO_2Et\cdot CH\colon CH\cdot C(CO_2Et)\colon N\cdot NH\cdot C_6H_3Me_2,$$

crystallises from dilute alcohol in pale yellow, glistening needles, m. p. 107°, and *ethyl* m-*xyleneazoglutacononate* m-*xylylhydrazone*,

$$C_6H_3Me_2\cdot N\colon N\cdot C(CO_2Et)\colon CH\cdot C(CO_2Et)\colon N\cdot NH\cdot C_6H_3Me_2,$$

in bright red, glistening prisms, m. p. 160—161°.

Ethyl 5-m-*xylyleneazo*-1-m-*xylyl*-6-*pyridazone*-3-*carboxylate*,

$$C_{23}H_{24}O_3N_4,$$

crystallises from alcohol in brilliant, brown prisms, m. p. 155° after sintering at 150°. *Ethyl glutacononate mesitylhydrazone*,

$$CO_2Et\cdot CH\colon CH\cdot C(CO_2Et)\colon N\cdot NH\cdot C_6H_2Me_3,$$

separates from dilute alcohol in yellow, glistening crystals, m. p. 79—80°. *Ethyl* 3-*mesityleneazoglutacononate mesitylhydrazone*,

$$C_{27}H_{34}O_4N_4,$$

separates from light petroleum in glistening, red crystals, m. p. 143—150°, and does not yield a pyridazone derivative. *Ethyl glutacononate* o-*phenetylhydrazone*,

$CO_2Et·CH:CH·C(CO_2Et):N·NH·C_6H_4·OEt$,

forms glistening, yellow crystals, m. p. 85°, and *ethyl* o-*phenetoleazo-glutacononate* o-*phenetylhydrazone*,

$OEt·C_6H_4·N:N·C(CO_2Et):CH·C(CO_2Et):N·NH·C_6H_4·OEt$,

crystallises from benzene in dark red, glistening prisms, m. p. 195°.

Ethyl p-*chlorobenzeneazoglutacononate* p-*chlorophenylhydrazone*,

$C_6H_4Cl·N:N·C(CO_2Et):CH·C(CO_2Et)·N:NH·C_6H_4Cl$,

crystallises in orange-coloured prisms, m. p. 138°, and when heated with alcohol yields *ethyl* 5-p-*chlorobenzeneazo*-1-p-*chlorophenyl*-6-*pyridazone-3-carboxylate*, $C_{19}H_{14}O_3N_4Cl_2$, as pale brown needles, m. p. 208—209° after sintering at 205°. *Ethyl* 3-m-*bromobenzeneazoglutacononate* m-*bromophenylhydrazone*, $C_{21}H_{20}O_4N_4Br_2$, also forms orange-coloured crystals, and has m. p. 130°; *ethyl* 5-m-*bromobenzeneazo*-1-m-*bromophenyl*-6-*pyridazone*-3-*carboxylate*, $C_{19}H_{14}O_3N_4Br_2$, forms pale brown, microscopic needles, m. p. 149°. The isomeric *o*-bromo-derivatives of the glutacononate and pyridazone compounds melt respectively at 143—144° and 166—167°, and the *p*-bromo-derivatives at 140° and 229°.

Ethyl glutacononate p-*nitrophenylhydrazone*,

$CO_2Et·CH:CH·C(CO_2Et):N·NH·C_6H_4·NO_2$,

forms a yellow, crystalline powder, m. p. 109°.

Formazyl-a-methylacrylic acid, $NHPh·N:C(N:NPh)·CH:CMe·CO_2H$, is formed by the action of benzenediazonium chloride (2 mols.) on methylglutaconic acid in dilute acetic acid solution (compare Abstr., 1908, i, 114), and crystallises from alcohol in dark-coloured needles, m. p. 193° (decomp.). It yields a sparingly soluble, reddish-brown, silver salt. J. J. S.

Decomposition of Azopyrazolones by means of Concentrated Nitric Acid. CARL BÜLOW, KARL HAAS, and, in part, with HERMANN SCHMACHTENBERG (*Ber.*, 1910, **43**, 2647—2662).—Rothenburg's 4-benzeneazo-3-methyl-5-pyrazolone (Abstr., 1895, i, 687) can be prepared by the condensation of hydrazine hydrate with ethyl phenylazoacetoacetate in acetic acid solution. Nitric acid reacts with this pyrazolone, yielding first an additive compound, $C_{10}H_{10}ON_4,2HNO_3$, and finally an orange-yellow nitro-derivative, which has been shown to be 4-*p*-nitrobenzeneazo-3-methyl-5-pyrazolone, as it can be synthesised from ethyl *p*-nitrophenylazoacetoacetate and hydrazine hydrate. Further reaction with nitric acid decomposes the nitroazopyrazolone derivative into Betti's 4-nitro-3-methyl-5-pyrazolone (Abstr., 1904, i, 533) and benzenediazonium nitrate. This decomposition, which proceeds according to the equation: $C_{10}H_{10}ON_4 + 2HNO_3 = H_2O + N_2PhNO_3 + C_4H_5O_3N_3$, is used in favour of the azo-structure of the original compound, since Schmidt (Abstr., 1905, i, 951) has shown that true azo-dyes react with concentrated nitric acid, yielding the diazo-compound used in the preparation of the dye, and a nitro-derivative of the compound, which was "coupled" with the diazo-solution. Knorr's

suggestion that the azo-derivatives of pyrazolone are hydrazones is thus incorrect.

Similarly, the products obtained by the action of diazonium salts on 3-substituted *iso*oxazolones (Claisen and Zedel, Abstr., 1891, 468) are azo-derivatives (*o*-hydroxyazo-compounds), as they are decomposed by nitric acid in acetic acid solution, yielding a diazonium nitrate and a nitro-derivative of the *iso*oxazolone, for example:

$$\begin{array}{l}O\cdot C(OH)\\ \vert\\ N{=\!=}CR\end{array}\!\!>C\cdot N{:}NR + 2HNO_3 = RN_2\cdot NO_3 + H_2O + \begin{array}{l}O\cdot C(OH)\\ \vert\\ N{=\!=}CR\end{array}\!\!>C\cdot NO_2.$$

Knorr's 4-nitro-1-phenyl-3-methyl-5-pyrazolone (Abstr., 1887, 601) and Betti's 4-nitro-3-methyl-5-pyrazolone are represented by hydroxylic and not ketonic formula; for example, the latter as

$$\begin{array}{l}NH\cdot C(OH)\\ \vert\\ N{=\!=}CMe\end{array}\!\!>C\cdot NO_2,$$

since the hydroxylic structure accounts for the pronounced acidic character of these nitro-compounds; for example, their alkali salts are neutral.

The primary product of the condensation of ethyl phenylazoacetoacetate and hydrazine hydrate in cold glacial acetic acid crystallises in glistening, red needles, m. p. 167°; when boiled with alcohol or glacial acetic acid it yields 4-benzeneazo-3-methyl-5-pyrazolone; when boiled with an acetic acid solution of phenylhydrazine it yields 4-benzeneazo-1-phenyl-3-methylpyrazolone, and when heated for a few minutes with an 80% acetic acid solution of benzhydrazide it yields ethyl phenylazoacetoacetate benzoylhydrazone, m. p. 146°. All these reactions indicate that the red compound is to be represented as $N_2H_2[CMe{:}C(N_2Ph)\cdot CO_2Et]_2$.

4-Nitro-5-hydroxy-3-methylpyrazole (4-nitro-3-methyl-5-pyrazolone) crystallises from acetic acid in prisms, m. p. 267° (decomp.), but cannot be acetylated. Its alkali salts are neutral, and hence the hydroxy-compound can be titrated by means of a standard alkali hydroxide solution, using phenolphthalein as indicator. The following salts are described: *potassium*, $C_4H_4O_3N_3K$; *ammonium*, yellow needles, decomposing at 248°; *hydrazine*, $C_4H_5O_3N_3,N_2H_4,H_2O$, glistening, yellow needles; *barium*, long, golden-yellow, compact prisms; *zinc*, yellow needles; *aluminium*, slender, yellow needles; *silver*, yellow plates, and also *copper*, *lead*, *cobalt*, and *nickel* salts.

4-Benzeneazo-5-hydroxy-3-methylpyrazole reacts with aqueous nitrous acid, yielding 4-*benzeneazo*-1-*nitroso*-5-*hydroxy*-3-*methylpyrazole*, $NPh{:}N\cdot C\!\!<\!\!\begin{array}{l}C(OH)\cdot N\cdot NO\\ \quad\quad\quad\ \ \vert\\ CMe{=\!=}N\end{array}$, which crystallises in slender needles, decomposing at 135°. The nitroso-group can be eliminated by warming for a short time with dilute sodium hydroxide solution, or with 15% hydrochloric acid, yielding the original hydroxypyrazole. The nitroso-compound is also decomposed when boiled with alcohol, acetone, or glacial acetic acid, and reacts with an excess of nitrous acid, yielding as final product 2 : 4-dinitrophenol.

When reduced with stannous chloride and hydrochloric acid 4-benzeneazo-5-hydroxy-3-methylpyrazole yields aniline and 4-*amino* 5-*hydroxy*-3-*methylpyrazole*, but the latter cannot be isolated on

account of the readiness with which it undergoes oxidation into a homologue of rubazonic acid, m. p. 238°.

The same acid is formed, together with a stable product, $C_4H_6O_2N_2$, by the action of oxidising agents on the reduction product of 4-nitro-5-hydroxy-3-methylpyrazole.

4-*m*-Xyleneazo-5-hydroxy-3-methylpyrazole also reacts with nitric acid, yielding 4-nitro-3-methylpyrazolone and *m*-xylenediazonium nitrate.

Nitric acid reacts with ethyl phenylazoacetoacetate, yielding ethyl *p*-nitrophenylazoacetoacetate. J. J. S.

Monosubstituted Triazens and Attempts to Prepare Triazen. OTTO DIMROTH and KARL PFISTER (*Ber.*, 1910, **43**, 2757—2767).—By the reduction of phenylazoimide by stannous chloride in ethereal solution, phenyltriazen is obtained (Dimroth, Abstr., 1907, i, 653). The reaction has been extended to substituted azides, some few of which are more stable than phenyltriazen, but the majority are less stable, decomposing on formation into amine and nitrogen. Benzylazoimide is much less easily reduced than phenylazoimide, and the triazen decomposes immediately on formation.

Attempts to reduce azoimide to triazen by a variety of methods were without success, but it is believed that triazen can exist for a short time in aqueous solution at −10°.

The reductions were carried out at −15° to −18° in dry ether, moisture being carefully excluded; the stannochloride of the triazen crystallises from the mixture, and can be kept without decomposition for some hours in a freezing mixture.

p-*Tolylazoimide* is an oil of characteristic anis-like odour, b. p. 80°/10 mm. o-*Bromophenylazoimide* is obtained pure on distillation in steam; o-*bromophenyltriazen* is extremely unstable; m-*bromophenylazoimide* has b. p. 99°/100 mm.; m-*bromophenyltriazen* is extremely unstable, and explodes on gentle heating.

p-*Bromophenyltriazen* is more stable; the *cuprous* compound,

$$C_6H_5BrN_3Cu,$$

forms yellow crystals, and explodes in the flame. The free triazen separates in long, colourless platelets when freshly prepared, m. p. 36·5°, decomposing into nitrogen and bromoaniline; older samples undergo a change manifested by a visible movement in the crystals, and have m. p. 39°. Solution in ether and precipitation with light petroleum gives the more fusible modification. Generally, *p*-bromophenyltriazen is more stable than phenyltriazen; when brought together with benzaldehyde in ethereal solution at −15°, it decomposes.

2 : 4 : 6-Tribromophenyltriazen could not be obtained from tribromophenylazoimide.

Similarly, *p*-methoxyphenylazoimide, which forms crystals, m. p. 36°, does not give a triazen on reduction.

Ethyl p-*azoimidobenzoate* is volatile in steam, and has b. p. 150°/10 mm., m. p. 18°. *Ethyl* p-*triazenobenzoic acid*, $C_6H_4(CO_2Et)\cdot N_3H_2$, forms a relatively stable stannochloride. The *cuprous* salt forms lustrous, golden platelets, decomp. 130°, and can be kept for some months. The free triazen crystallises in lustrous granules or feathery needles, m. p. 68° (decomp.). It conbines with phenyl cyanate to an *azocarbamide*,

$CO_2Et\cdot C_6H_4\cdot N\colon N\cdot NH\cdot CO\cdot NHPh$, which crystallises in colourless, lustrous, thin, six-sided plates, m. p. 135° (decomp.). It dissolves in dilute sodium hydroxide with an intense yellow coloration, forming on the addition of acetic acid the *carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot N\colon N\cdot NH\cdot CO\cdot NHPh,$$

crystallising in colourless needles, m. p. 172°.

With formaldehyde, the triazen condenses to form a *compound*,

$$CO_2Et\cdot C_6H_4\cdot N_2\cdot NH\cdot CH_2\cdot NH\cdot N_2\cdot C_6H_4\cdot CO_2Et,$$

decomp. at 48° to ethyl methylenedi-*p*-aminobenzoate, m. p. 188°.

p-*Benzoylphenylazoimide* crystallises in pale yellow, lustrous plates, m. p. 74·5°. The corresponding triazen is relatively stable; it dissolves in ether without the formation of gas, and can be kept in a desiccator for a day.

α- and *β*-Naphthylazoimides did not yield triazens on reduction.

E. F. A.

Ionisation, Hydration, and Optical Rotation of White of Egg. Wolfgang Pauli (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 241—243).—The author gives a brief summary of observations which indicate that egg-albumin behaves as a weak amphoteric electrolyte. The properties of acid and alkaline solutions seem to show that the positive and negative albumin ions are combined with a very large number of molecules of water. The hydration which accompanies ionisation gives rise to considerable differences in the optical rotatory power and the viscosity of egg-albumin solutions. The readiness with which albumin ions are formed by different acids is not simply determined by the relative strengths of the acids, although this appears to be the case for the formation of negative ions on addition of different mono-acid bases.

The phenomenon of ionic hydration, which is so strongly developed in the case of albumin, is supposed to be analogous to that of gelatinisation.

H. M. D.

General Protein Chemistry. II. Precipitation of Globulins at the Isoelectric Point. Peter Rona and Leonor Michaelis (*Biochem. Zeitsch.*, 1910, **28**, 193—199. Compare this vol., i, 646).—It was shown in a previous paper that the sedimentation rate of denatured albumin attains a maximum when the hydrogen ion concentration is that of the isoelectric point, and the same is now shown to be the case for solutions of ordinary (not denatured) serum-globulin, edestin, gliadin, and casein. On this behaviour is based a clear distinction between globulins and albumins; the former are "denaturable" proteins, which, in the ordinary form, precipitate from solution at the isoelectric point, whereas the albumins in the ordinary form are not precipitated by acids, but when denatured also have their sedimentation optimum at the isoelectric point.

The isoelectric constants and relative acidity constants at 18° are as follows: Serum globulin, $0·36\times10^{-5}$, $2·2\times10^{3}$; casein from cow's milk, $1·8\times10^{-5}$, $5·4\times10^{4}$; gliadin, $6·0\times10^{-10}$, $6·0\times10^{-5}$; edestin, $1·3\times10^{-7}$, 2·8, as compared with albumin $0·31\times10^{-3}$, $1·6\times10^{3}$. Serum-globulin from different animals gave the same values. G. S.

Composition of Nucleic Acid from Yeast. KATHARINA KOWALEVSKY (*Zeitsch. physiol. Chem.*, 1910, **69**, 240—264. Compare Levene, Abstr., 1909, i, 54).—Nucleic acid has been prepared from yeast by Altmann's (*Arch. physiol.*, 1899, 526) and by Neumann's method (Abstr., 1899, i, 467; 1900, i, 319), but the product obtained by the latter method is shown to be very impure. The analysis of four specimens prepared according to Altmann gave as a mean N = 12·32% and P = 10·02%. The low nitrogen value indicates that nitrogenous bases had been removed by acid during the preparation. A specimen prepared on a commercial scale gave N = 16·16% and P = 8·65%, and this was used for hydrolysis.

When hydrolysed with nitric acid (10 c.c. of nitric acid, D 1·4, + 10 c.c. of water), the products obtained were guanine, 5·16%; adenine, 7·36%; with sulphuric acid (1 : 2) the products were guanine, adenine, cytosine, and uracil, but no thymine. The uracil is regarded as a secondary product. The nitrogenous portion of the nucleic acid consists of guanine, adenine, and cytosine. The non-nitrogenous portion contains a pentose and not a hexose. The product, C_7H_8O, isolated by Boos (Abstr., 1909, i, 343) in the form of its phenylhydrazone is benzaldehyde, and was present as an impurity in the original phenylbenzylhydrazine used. On the assumption that a molecule of pentose and one of phosphoric acid is present for each molecule of base, the formula $C_{29}H_{42}O_{23}N_{13}P_3$ ($C_5H_5ON_5 + C_5H_5N_5 + C_4H_5ON_3 + 3C_5H_{10}O_5 + 3H_3PO_4 = C_{29}H_{42}O_{23}N_{13}P_3 + 6H_2O$) can be deduced. The amounts of bases and pentose actually isolated are less than those required by such a formula, with the exception of guanine. J. J. S.

Guanylic Acid. IVAR BANG (*Zeitsch. physiol. Chem.*, 1910, **69**, 167—168).—Polemical. The author defends his formula for guanylic acid, $C_{44}H_{66}O_{34}N_{20}P_4$, against that proposed by Steudel and Brigl, $C_{10}H_{14}O_8N_5P$. W. D. H.

Protamines. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1910, **69**, 138—142).—*Crenilabrine* is a new protamine separated from the testes of *Crenilabrus pavo*. It yields arginine nitrogen, 42·3%; lysine nitrogen, 11%, and monoamino-nitrogen, 25·1%. Ammonia, tryptophan, and histidine are absent from its cleavage products. It gives Millon's reaction, so tyrosine is probably present. It is therefore not so simple as salmine.

Malenük has prepared sturine from the Caspian sturgeon; the material appears to have suffered in transport, and Malenük has somewhat modified the author's method; he, moreover, found adenine among the cleavage products, which was not the case with sturine made from German sturgeons. W. D. H.

Lipoids. XIV. Leucopoliin. SIGMUND FRÄNKEL and HERBERT ELIAS (*Biochem. Zeitsch.*, 1910, **28**, 320—329).—From the acetone extract of human brain, a new phosphatide named *leucopoliin*, was separated. It is crystalline, and of constant composition, the formula of its cadmium compound being $C_{374}H_{720}O_{74}N_{10}P_2Cl_4Cd$. It is a deca-amino-diphosphatide, or a penta-amino-monophosphatide. It contains no

methyl group, and yields no base of the choline group. It contains a carbohydrate acid nucleus. It occurs in about equal quantities in white and grey matter, hence its name. W. D. H.

Invertase. HANS VON EULER, E. LINDBERG, and K. MELANDER (*Zeitsch. physiol. Chem.*, 1910, **69**, 152—166).—A certain quantity of yeast always yields the same amount of invertase whether the dried material is extracted with water, or autolysis is allowed to occur. The preparation of invertase obtained in autolysis contained N 0·36%, C 42·3%, and ash 2·07%. It is the most active preparation so far obtained. If 0·05 gram is dissolved in 5 c.c. of 0·5*N*-sodium dihydrogen phosphate, and 20 c.c. of 20% sucrose solution are added, rotation 0° is reached at room temperature (20°) in fourteen minutes. W. D. H.

Enzymes of Diastase. L. M. LJALIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 624—633).—The enzymes in various kinds of malt were obtained by precipitation with ammonium sulphate, and the activity of the various preparations in the breaking down of starch was determined as follows: 10 c.c. of a 10% emulsion of starch were placed in a test-tube, the latter immersed in boiling water for half a minute and shaken. After cooling to 20°, a given quantity (0·1, 0·2 . . . c.c.) of the diastase preparation was added, the tube well shaken, and left for half an hour at 20°; 1/2 c.c. of magenta is now added, and the tube inverted. The starch in the tubes in which the magenta is spread evenly through the solution has been completely broken up. The diastase precipitated with ammonium sulphate is always more active than that precipitated with alcohol, and the diastase from air-dried malt, green malt, and the light-coloured malts employed in the manufacture of light beer are the most active, whilst that from dark malt dried at a high temperature is least active.

The fermenting, coagulating, and proteolytic enzymes as well as the oxydases in the diastase obtained from these and other substances are all of the same order of activity according to the source from which they are prepared. Z. K.

The Deviation of Ferment Action from the Unimolecular Law, with Especial Reference to the Esterases. GEORGE PIERCE (*J. Amer. Chem. Soc.*, 1910, **32**, 1517—1532).—The rate of hydrolysis of ethyl butyrate under the influence of lipase has been measured at 37° for different concentrations of the ester and the enzyme. In some experiments the progress of the reaction was found to be in satisfactory agreement with the equation for a unimolecular change, but this is not generally the case, and the actual course in a particular experiment appears to be determined by the relative concentrations of ester and enzyme. Another factor which is of importance is the acid produced by the hydrolysis, for this apparently diminishes the activity of the enzyme.

In solutions which contain the same amount of ester and acid, the time required for the hydrolysis of a given quantity of ethyl butyrate is inversely proportional to the concentration of the enzyme. For

given enzyme and acid concentrations, the time required for the decomposition of the same amount of ester is independent of the ester concentration, provided that this exceeds a certain limiting value. It thus appears that the activity of the enzyme is independent of the ester concentrations where this is varied between considerable limits.

To account for the observations, it is supposed that the enzyme combines with the ester to form an intermediate compound, the amount of which is proportional to the concentrations of the free enzyme and the ester. This compound then undergoes hydrolysis in accordance with the mass action law.

It is shown that the observed facts are consistent with this hypothesis, and that the action is similar to that which probably takes place in the inversion of sucrose under the influence of invertase.

H. M. D.

Benzophosphide. PERCY N. EVANS and JENNIE TILT (*Amer. Chem. J.*, 1910, 44, 361—365).—Evans and Vanderkleed (Abstr., 1902, i, 273) have described dichloroacetyl phosphide,

$$CHCl_2\cdot CO\cdot PH_2,$$

and an account is now given of the preparation and properties of benzoyl phosphide, $C_6H_5\cdot CO\cdot PH_2$. In view of the analogy of these compounds to the amides, it is suggested that they would preferably be termed "dichloroacetophosphide" and "benzophosphide."

Benzophosphide, prepared by treating benzoyl chloride for six weeks with a current of dry phosphine, generated by the action of phosphorus on alcoholic potassium hydroxide, forms a slightly yellow, or sometimes white, powder. It does not give a definite m. p., but begins to decompose at about 125°. When heated in a current of dry nitrogen, it gradually decomposes above 75° with evolution of phosphine. It is slowly attacked by water or moist air.

E. G.

Action of Arsenic Acid on Gallic Acid. LEO F. ILJIN (*J. pr. Chem.*, 1910, [ii], 82, 451—462).—Walden, (Abstr., 1899, i, 212) supports Schiff's statement that digallic acid is one of the products of the reaction between gallic and arsenic acids in 95% alcoholic solution. The author has repeated Walden's experiment, but cannot obtain digallic acid, the product free from arsenic being separable by ethyl acetate and petroleum into two fractions, neither of which exhibits the properties of digallic acid; one fraction consists of gallic acid, the other (the smaller) of ethyl gallate.

With regard to the organic arsenic compounds formed in the preceding reaction, the author's results differ from those of Biginelli (Abstr., 1909, i, 801). The arsenical substance obtained by the author in the preceding experiment can be separated, in aqueous ethereal solution, into two fractions by the addition of sodium chloride, one of which does, and the other does not, yield a precipitate with a solution of gelatin. The former is still under investigation; the latter is obtained, after purification, in long needles of the composition $(C_9H_9O_5)_3AsO$.

C. S.

// JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Photometric Measurements with the Coloured Bunsen Flame. ERNST BECKMANN and PERCY WAENTIG (*Zeitsch. physikal. Chem.*, 1909, **68**, 385—439).—A new arrangement for supplying salts to a flame, which gives constant and readily reproducible results, is described and figured. A salt solution is allowed to drop on a disk kept in rapid rotation, and the fine-spray thus produced is carried away by the stream of gas, drops of liquid being retained. The different factors determining the properties of the flame, more particularly the velocity of rotation of the disk, the rate of supply of the salt solution and of the gas, can be varied independently, and the effect of each is described in detail. The method of determining the amount of salt supplied to the flame depends on the property of the silent electric discharge in condensing dust particles; for this purpose the gas charged with salt particles is passed through a Siemens' ozone tube, and the salt deposited after a considerable interval removed and weighed.

The effect of anions on the intensity of the flame was determined by measurements with a König-Martens-Grünbaum photometer. For the alkali metals, the salts of oxygen acids give a rather more intense flame than the halogen salts, but hydrogen peroxide does not appreciably increase the intensity. As regards the alkaline earth metals, the intensity for the halogen salts of calcium is greater than for

the salts of oxygen acids, but barium salts show the converse behaviour. In the case of strontium and lithium salts, change of the anion alters even the tint of the flame.

Foreign salts, including both those which colour and do not colour the flame, diminish the intensity of the colour, and both anion and cation seem to take part in this effect. The diminution increases with increasing proportion of the salt added, and the effect appears to be the greater the higher the equivalent weight of the cation.

Accurate measurements have been made on the relationship between the concentration of the salt solution and the amount of salt conveyed into the flame. For the solution of a single salt, the ratio between the salt sprayed and the concentration of the salt solution is constant, but for mixtures of salts, especially in concentrated solution, the amount converted into spray is relatively smaller. According to Arrhenius (Abstr., 1891, 5, 515) and Gouy (*Ann. Chim. Phys.*, 1879, [v], **18**, 5), the intensity of the colour in the flame and the electrical conductivity are proportional to the square root of the concentration of the salt in the flame. The authors find, however, that these laws hold only for certain salts under certain definite conditions. On the other hand, the effect of the anions on the intensity is parallel to that on the electrical conductivity, and there is doubtless a close connexion between luminosity and electrical conductivity. G. S.

Spectral Analytical Investigation of the Glow Light at Points. HERMANN VON DECHEND (*Ann. Physik*, 1909, [iv], **30**, 719—745).—The spectra of the glow which accompanies electric discharge between points have been investigated. The discharge was allowed to take place between platinum and aluminium electrodes in tubes containing different gases.

In the case of oxygen, nitrogen, and chlorine, the point discharge spectrum is similar to that obtained by the use of Geissler tubes. With nitrogen, nitric oxide, and air, which all show the first banded spectrum of nitrogen, the light emission is not confined to the immediate neighbourhood of the points, but is spread out through the space between the electrodes. Hydrogen also exhibits a second luminous region, and this takes the form of a luminous stream of negatively charged ions, which are emitted from the cathode in a direction which is independent of the position of the anode. The spectrum of this luminous stream consists of indistinct lines which do not coincide with the lines of any known spectrum. On the other hand, the spectrum of the glow at the points consists of the first and second hydrogen spectra.

Observations were also made with hydrogen chloride, methane, carbon monoxide, and carbon dioxide. All these gases are decomposed by the point discharge. Hydrogen chloride shows the stronger chlorine lines, some of the hydrogen lines, and also a continuous spectrum. Methane exhibits hydrogen lines and the Swan spectrum. Carbon monoxide and carbon dioxide, which give the same Geissler tube spectrum, behave differently in the case of point discharge. The former shows all the chief bands of the carbon monoxide spectrum, whilst the latter only gives the band at 4123. H. M. D.

Band Spectra of Barium and Aluminium. P. E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1909, **149**, 899—903. Compare Trans., 1909, **95**, 279).—The author believes that the bands in the spectra of salts of barium and aluminium are due to the metals (compare Börsch, Abstr., 1909, ii, 775), and that they result from disturbances of the simpler vibrations which are predominant at high temperatures. Certain relations which hold between the frequencies of the right, that is, the most refrangible, edges of the bands of barium and aluminium are also developed. T. S. P.

Systems of Series in the Spectra of Zinc, Cadmium, and Mercury. FRIEDRICH PASCHEN (*Ann. Physik*, 1909, [iv], **30**, 746—754).—An examination of the data of various observers shows that the spectra of zinc, cadmium, and mercury contain three series of lines which are analogous to those found in the spectrum of magnesium. H. M. D.

Influence of Dilution on the Colour and the Absorption Spectra of Various Permanganates. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1909, **15**, 247—256).—The author has compared the photographs of the absorption spectra of aqueous solutions of barium, zinc, and potassium permanganate containing 0·001 gram-molecule per litre and of solutions prepared from these by diluting 30·8 and 62 times respectively. The freshly prepared solutions exhibit differences in the width of the bands and also in the amount of general absorption, at the more refrangible end of the spectrum. On keeping, the two series of diluted solutions exhibit changes in colour which are accompanied by changes in the width of the bands and an increase in the general absorption. In the case of the most dilute series, the brownish-yellow colour which is developed is attended by an almost complete obliteration of the absorption bands. The observed changes take place whether the solutions are insolated or kept in the dark, but the rate of change is increased by light. The changes in colour are supposed to be due to a decomposition of the permanganate ions under the influence of the solvent. H. M. D.

Relations between Constitution and Absorption towards the Violet End of the Spectrum for Solutions of certain Chromium and Iron Salts. ALFRED BYK and H. JAFFE (*Zeitsch. physikal Chem.*, 1909, **68**, 323—356).—The observations were made with an instrument provided with quartz lenses and prisms, and the spectra were photographed. The limits of absorption for the different solutions are given in tabular form. Most of the chromium salts were used in dilutions from $\frac{1}{2}$ to $\frac{1}{10}$ molar, but the iron salts were used also in much greater dilution.

All the solutions of violet chromium salts show similar absorption (absorption band $461\mu\mu$ to $364{\cdot}5\mu\mu$; beginning of complete absorption about $260\mu\mu$ in $\frac{1}{2}$ molar solution), which is therefore due to the chromium ion. The band becomes narrower with increasing dilution. Slight deviations with the nitrate are doubtless due to the absorption of the NO_3' ion.

In solutions of green, complex chromium salts the absorption band and the limit of complete absorption are both shifted towards the red end of the spectrum. Each solution has, however, its own individual spectrum, and the more completely the electrons are displaced by radicles the greater is the displacement towards the red end. For the influence of acids (added to the green solutions) on the spectra, which is somewhat complicated, the original paper must be consulted.

Neutral concentrated solutions of ferric alum and of ferric nitrate are reddish-brown, the corresponding solutions of ferric chloride are yellowish-brown, and there are corresponding differences in the absorption spectra. Hydrochloric acid darkens the colour of ferric chloride solutions, probably owing to the formation of the complex $FeCl_3$, which has greater absorbing power than the ion $Fe^{\cdot\cdot\cdot}$. The addition of sulphuric acid lightens the colour of iron alum, a result probably connected with diminution of hydrolysis. In very dilute solutions, on the other hand, the addition of sulphuric acid increases the absorption, probably owing to the change of $Fe^{\cdot\cdot\cdot}$ ions to complex ions. Ferric chloride has greater absorption than the fluoride, corresponding with the greater weight of the chlorine atoms.

With increasing dilution, ferrous salts show more distinctly the absorption characteristic of $Fe^{\cdot\cdot}$ ions.

For all the salts examined, non-ionised chlorides have greater absorbing power than the corresponding sulphates. G. S.

Relationship between the Colour and Constitution of Unsaturated Ketones and their Salts. HANS STOBBE, RICHARD HAERTEL, and SIEGFRIED SEYDEL (*Annalen*, 1909, **370**, 93—99, 99—129, 129—141).—See this vol., i, 43, 45.

Polychroism of Artificially Coloured Crystals. PAUL GAUBERT (*Compt. rend.*, 1909, **149**, 1004—1006).—The author has previously shown that artificially coloured crystals may be polychoic, and that they may be divided into two classes. In the first class the colouring matter is in a state of solution in the crystals, whilst in the second class it exists in the form of crystals, the orientation of which may be different from that of the crystal occluding them. Lehmann has put forward the idea that there is a relation between the intensity of the polychroism and the double refraction of a coloured crystal. The author shows that this only holds for crystals belonging to the first class. In crystals of phthalic acid, meconic acid, carbamide nitrate, carbamide oxalate, phloridzin, and chrysotile, coloured by methylene-blue, which belong to the first class, the differences between the amounts of light absorption in the two optical axes increase with the amount of double refraction.

Crystals, such as lead nitrate and barium nitrate, when coloured with methylene-blue belong to the second class. They show an intense polychroism, although they are only very feebly doubly refracting.

The connexion between polychroism and double refraction, as indicated above, may be used to classify other coloured crystals.

T. S. P.

Luminescence Phenomena in Certain Organic Compounds. ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 358—365).—It is stated in the text-books that no phosphorescent liquid is known, with the possible exception of liquid oxygen. But the author has shown previously (*ibid.*, 1905, [v], **14**, ii, 222) that the mineral oil usually employed in Geryk pumps (which in ordinary light exhibits a marked greenish-yellow fluorescence) gives under the influence of cathode rays a vivid dark blue luminescence, which disappears sensibly at the same time as the excitation ceases; similar luminiscence is obtained with the oil after solidification at the temperature of liquid air, but in this case it persists five to ten seconds after the cessation of the cathode rays. The influence of the state of aggregation on the luminescence is also shown by ordinary wax, which, when solid, exhibits a pale yellowish-sky-blue, and, when liquid, a dark blue, cathodic luminescence.

The luminescence effects of anthracene, phenanthrene, fluorene, and retene were studied in four tubes: (1) a cathode ray tube, (2) an anode ray tube, (3) a horizontal tube with symmetrical plane electrodes, and (4) a tube in which the distance between substance and cathode can be varied, the change of state being effected by the thermal action of the cathode rays themselves.

Also in tube (1) the following substances, all capable of exhibiting ordinary fluorescence in suitable solutions, were examined: alizarin, phthalic anhydride, anthranilic acid, rhodamine, α- and β-naphthylamines, α- and β-naphthols, phthalimide, euphosphine, aminonaphtholdisulphonic acid, β-naphthol-β-sulphonic acid, vaselin, and naphthalene.

The luminescence emitted by the monoclinic laminæ of anthracene or phenanthrene, or by the trimetric prisms of phthalic anhydride or α-naphthylamine, shows no appreciable polarisation. The behaviour of the above substances in the vacuum tubes indicates that with most of them the state of aggregation exerts a marked influence on the colour of the cathodic luminescence, the colour changing at the moment of fusion and changing again to the original one on re-solidification. Then, too, certain of the substances are luminescent only when either liquid or solid. The changes of colour as the degree of evacuation is increased are also discussed. T. H. P.

Phosphorescence of some Inorganic Salts. JOHN ANDERSON WILKINSON (*J. Physical Chem.*, 1909, **13**, 691—728).—Experiments are described which show the existence of a relationship between phosphorescence and chemical action. When aqueous solutions of chlorides, bromides, iodides, and sulphates are electrolysed with anodes of copper, mercury, silver, cadmium, zinc, potassium, and sodium, the salt formation at the anode is in many cases accompanied by the emission of light, the colour of which in most cases resembles that of the fluorescent and phosphorescent light emitted under the influence of cathode rays.

Similar luminous effects are also obtained when the metals enter into direct combination with the halogens or oxygen at elevated

temperatures. In the case of sodium and potassium, the colour of the light emitted varies with the rate of combination. The colour of the phosphorescent light corresponds with that emitted when slow combination takes place.

Certain salts, said to be phosphorescent, were found not to be so when pure, but phosphorescence could be induced by the addition of small quantities of other salts. Sodium peroxide shows fluorescence and phosphorescence under the action of cathode rays if a good vacuum is maintained. The fluorescence of aluminium oxide under the same conditions is traced to the presence of sodium in the form of peroxide or the aluminate. H. M. D.

Electrical Behaviour of Fluorescing Iodine Vapour. R. WHIDDINGTON (*Proc. Camb. Phil. Soc.*, 1909, **15**, 189).—A beam from an arc light was focussed on iodine vapour between two copper electrodes. Although fluorescence was plainly visible, no trace of ionisation could be detected even when the applied electric field was almost sufficient to produce discharge. The experiment shows that fluorescence is not necessarily accompanied by ionisation.

H. M. D.

Optical Activity of the Asymmetric Atom. A. E. EVEREST (*Chem. News*, 1909, **100**, 295).—Perkin, Pope, and Wallach have recently resolved 1-methyl-Δ^3-*cyclo*hexylidene-4-acetic acid into two enantiomorphous forms, and claim that in this case optical activity is due to enantiomorphous, molecular configuration and not to the presence of an asymmetric atom (Trans., 1909, **95**, 1789). The author contends that the carbon atom numbered 1 in the formula given in the original paper (*loc. cit.*, 1792) is asymmetric by reason of its position in relation to the H– and $-CO_2H$ groups marked *c* and *d* respectively in the same formula. *p*-Methyl*cyclo*hexylcarboxylic acid at first sight appears to contain two asymmetric carbon atoms, as here defined, but this apparent analogy disappears when it is remembered that the –H and CO_2H- groups (and also the –H and $-CH_3$ groups occupying similar positions in relation to the carbon atom marked 4) in the original formula (*loc. cit.*) in this case are in a plane at right angles to the ring. T. A. H.

Attempts at Asymmetric Synthesis by means of Circularly-polarised Light. MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 390—392).—The action of bromine on a carbon disulphide solution of angelic acid under the influence of circularly-polarised light yields only optically inactive products (compare Wislicenus, Abstr., 1893, i, 135, 455; Cotton, Abstr., 1909, ii, 278). T. H. P.

Photochemical Action. II. EMIL WARBURG (*Ber. Deut. physikal. Ges.*, 1909, 654—660. Compare *ibid.*, 1907, 753).—The transformability of radiant energy is considered with reference to a gas which is photochemically sensitive, and in which the photochemical change can also be brought about by a change of temperature. If T_1 and T_2 denote respectively the temperature of the gas and that

corresponding with the incident radiation, T_3 the temperature corresponding with the shift of the equilibrium between the gas and its products of dissociation consequent on the absorption of the radiant energy, Q_2 the amount of energy absorbed, and q the heat of formation of the gas from its dissociation products, then it is shown that $q/T_3 - Q_2/T_2 + (Q_2 - q)/T_1 \geqq 0$. If the whole of the absorbed energy is used up in the chemical transformation, then $Q_2 = q$ and $T_3 \leqq T_2$. According to this relationship, the chemical decomposition of the photochemically sensitive gas reaches a limit when the change in the concentration of the products of dissociation has reached a point which corresponds with the temperature of the incident radiation. The application of the deduced relationship to the dissociation of carbon dioxide and the conversion of oxygen into ozone is considered.

H. M. D.

Apparatus for Measuring Radioactivity. BÉLA SZILÁRD (*Compt. rend.*, 1909, **149**, 912—914).—The gold leaf of the electroscope is replaced by a steel needle, mounted horizontally. The needle is magnetised, and in the zero position it lies in the magnetic meridian. When in this position it is encased by a metallic ribbon, with which it is connected electrically. The whole is mounted in a box fitted with a plate and ring of soft iron, in order to screen the needle from external influences. The deviation of the needle is a measure of the charge given to the system when, for example, a radioactive substance is introduced into the box. The whole apparatus is portable.

T. S. P.

The Scattering of the β-Rays of Radium. JOHN P. V. MADSEN (*Phil. Mag.*, 1909, [vi], **18**, 909—915. Compare Crowther, Abstr., 1908, ii, 247).—These results confirm the experiments of Crowther with the β-rays of uranium. The scattering of the β-rays of radium by thin films of material has been found to be unsymmetrical about a plane at right angles to the direction of the radiation, more emerging in the original direction than are returned. Gold turns back a greater proportion of the scattered radiation than aluminium. The emergent scattered radiation attains a maximum with 0·013 cm. aluminium and 0·0008 cm. gold. There is thus a close parallel between the scattering of β- and γ-rays (Madsen, Abstr., 1909, ii, 365), which is in support of Bragg's discrete or neutral-pair theory of the γ-rays. The results of McClelland on secondary β-rays (Abstr., 1908, ii, 651) are regarded as explicable without the need of supposing that there exists a true secondary radiation proceeding from the atoms affected by incident β-rays.

F. S.

Passage of β-Rays through Matter. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1909, **10**, 929—948).—Experiments have been made to determine whether the absorption of β-rays takes place exactly according to an exponential law. In order that this may be the case, it is necessary that the penetrating power of homogeneous β-rays should be constant and independent of the thickness of matter traversed.

Measurements were made on the β-rays emitted by radium-E and by uranium-X. These were allowed to fall on metal plates, and the penetrating power of the incidence and emergence radiation was compared.

From the experimental results, the conclusion is drawn that β-rays experience a slight diminution in velocity in their passage through matter. The magnitude of this diminution increases as the atomic weight of the traversed substance decreases. It also increases with the extent to which the β-rays are diverted from their original direction of movement. In accordance with this, it is found that for thin layers of material, the amount of transmitted β-radiation diminishes more quickly than corresponds with an exponential law. This is equivalent to a diminution in the penetrating power as the thickness of the absorbing material increases.

In addition to various metals, the absorption of the β-rays in gases was also examined. In comparison with air, hydrogen is found to be very highly ionised by the β-rays. This is in agreement with the general result that elements of low atomic weight have a relatively large absorption capacity. H. M. D.

Law of Absorption of the β-Rays. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1909, **10**, 948—950).—The conclusions drawn by Wilson (*Proc. Roy. Soc.*, 1909, *A*, 82, 612) from an investigation of the absorption of homogeneous β-rays are opposed to the results obtained by the authors in similar measurements. A critical examination of the experimental arrangement adopted by Wilson shows that the rays examined were not homogeneous, and that his conclusions are therefore untenable. H. M. D.

Phenomena of X-Ray Transmission. CHARLES G. BARKLA (*Proc. Camb. Phil. Soc.*, 1909, **15**, 257—268).—The relationships between the various phenomena which accompany the transmission of Röntgen rays are discussed. It is shown that there is an intimate connexion between the absorption of the primary radiation in a substance, the ionisation in the absorbing substance (when in the gaseous state), and the intensity of the secondary radiation from the absorbing substance. These are periodic functions of the penetrating power of the primary radiation, the three rising and falling together. The periodicity in intensity of the secondary radiation is not one of intensity alone, for each fresh period brings a characteristic radiation of different penetrating power. H. M. D.

Alteration in the Colour of the Diamond under the Action of Various Physical Agents. PAUL SACERDOTE (*Compt. rend.*, 1909, **149**, 993—994. Compare Abstr., 1906, ii, 863; 1907, ii, 956).—Diamonds varying in colour from colourless to a greenish-yellow have been submitted successively to the action of X-rays, cathode rays, and a temperature of 300—400°. The duration of the experiments varied from some minutes to a few days.

X-rays have no sensible effect on the colour. Cathode rays gradually deepen the initial colour (colourless diamonds become coloured)

through a wine-red to a more or less deep brown, depending on the time of action. The colours so obtained seem to be stable, since diamonds so coloured have been kept for a year or so.

Exposure to a temperature of 300—400° rapidly converts the diamond to its original colour. T. S. P.

Influence of Radium *X*-Rays and Cathode Rays on Various Precious Stones. ANDRÉ MEYÈRE (*Compt. rend.*, 1909, **149**, 994—995).—Diamonds and different varieties of corundum (sapphire, white sapphire, ruby) have been submitted to the action of *X*-rays, cathode rays, and of radium. In some cases the stones were placed outside the *X*-ray tube; in other cases they were submitted to the action of *X*-rays and cathode rays by being placed inside the tube. For the electrodes of the tubes, different combinations of copper, nickel, aluminium, and platinum were used, and in all experiments the vacuum in the tube was maintained by the continuous working of a mercury pump. In some experiments the current was only passed at intervals of some seconds, in order to avoid heating the stones.

In all cases the corundums and diamond become more or less brown in colour (compare preceding abstract). T. S. P.

Influence of Radium Rays on the Coloration of Sanidin, Zircon, and Quartz. Crystalline Form of the Zircon in Sanidinite from the Laacher See. R. BRAUNS (*Centr. Min.*, 1909, **23**, 721—728).—Observations are recorded which show that certain naturally colourless forms of zircon are coloured when subjected to the action of radium. A similar effect is also found in the case of certain coloured varieties of zircon and quartz which have been decolorised by heating. On the other hand, colourless zircon from Pfitsch and colourless quartz are unacted on by radium. The colour effects are attributed to the presence in the minerals of foreign substances which are acted on by radium rays. Crystallographic measurements of two forms of zircon occurring in the sanidinite of the Laacher See are recorded. H. M. D.

Accumulation of Helium in Geological Time. II. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1909, *A*, **83**, 96—99. Compare Abstr., 1908, ii, 922).—The amount of helium in ironstones from various localities has been determined. The results are given in terms of the "helium ratio," which expresses the amount of helium in c.c. per gram of total equivalent uranium oxide. It is found that one gram of thoria is equivalent to 0·203 gram of uranium oxide so far as the production of helium is concerned, and the expression "total equivalent uranium oxide" represents therefore the quantity of uranium oxide plus 0·203 time the quantity of thoria in a mineral. The helium ratio thus defined is found to vary from 0·76 to 13·3.

With regard to the rate of formation of helium from the uranium and thorium series of substances, direct measurements have given $10{\cdot}4 \times 10^{-8}$ c.c. per gram of uranium oxide per annum. This is in good agreement with Rutherford's indirectly obtained value of

$9 \cdot 13 \times 10^{-8}$ c.c. No accurate value has yet been obtained for the thorium series, but the rate is certainly smaller than in the case of uranium. H. M. D.

The Relation between Uranium and Radium. IV. FREDERICK SODDY (*Phil. Mag.*, 1909, [vi], **18**, 846—858. Compare Abstr., 1908, ii, 919).—The three uranium solutions purified by Mackenzie in 1905–1906 have all shown during the past year an increase in the quantity of radium present. The methods of measuring the radium have been improved in detail, and are now accurate to about 10^{-12} gram. The rate of growth of radium in all three solutions has been proportional to the square of the time since purification. In the oldest solution, containing 250 grams of uranium, the radium in the last year has increased from 19·6 to 24·3 ($\times 10^{-12}$ grams). The period of average life of the intermediate substance (ionium) is calculated to be 18,500 years, assuming there is only one. The existence of a new relatively short-lived intermediate product in the series is indicated, retarding still further the rate of growth of radium initially. Such a substance, if it exists, would reduce the period above referred to, which is therefore a maximum estimate. F. S.

The Rays and Products of Uranium-*X*. FREDERICK SODDY (*Phil. Mag.*, 1909, [vi], **18**, 858—865. Compare Abstr., 1909, ii, 459, 460).—On the view that the direct parent of radium is the direct product of uranium-*X*, powerful preparations of the latter should develop a feeble α-radiation as the uranium-*X* disintegrates and its β-radiation decays. From the maximum period of the parent of radium (compare preceding abstract) it is calculated that the uranium-*X* in equilibrium with 1 kilogram of uranium should give a product having the α-activity of 2 mg. of uranium. This it has been now shown not to do. Measurements of the α-activity of several preparations of uranium-*X*, prepared from 50 kilos. of uranyl nitrate, in an intense magnetic field in hydrogen to minimise the powerful β-radiation, have shown in all the presence of a constant feeble α-radiation from the start, due apparently to a substance genetically unconnected with uranium-*X*, but separated with it (possibly ionium). The earlier observations of a rapid growth of α-rays (Abstr., 1909, ii, 460) have not since been confirmed by more perfect methods and are rejected. The conclusion arrived at is that the direct parent of radium cannot be the direct product of uranium-*X*, and it is doubtful whether it can be a product at all. The difficultly deviable β-radiation of uranium-*X* appears to resemble ordinary β-rays, but shows an anomalous behaviour in certain respects. F. S.

Experimental Study of the Large Ions in the Air. S. G. LUSBY (*J. Roy. Soc. New South Wales*, 1909, **43**, 55—60).—Measurements have been made of the mobility of the slowly-moving ions which are present in the air, and also of the removal of these ions under the influence of drying agents and the rate at which they are reproduced. The apparatus is similar to that described previously by Zeleny. The number of the large ions, as well as of the small

ions, is considerably reduced when the air is passed over calcium chloride or phosphoric oxide before it enters the testing apparatus. The reduction amounts to 50% when the air is dried as completely as possible by passing over a sufficiently long column of phosphoric oxide. If the large ions are completely removed by an electric field, it is found that an interval of about twenty-two minutes elapses before the number of ions in unit volume attains its original value.

H. M. D.

Mobility of the Large Ions in the Air. JAMES A. POLLOCK (*J. Roy. Soc. New South Wales*, 1909, **43**, 61—68. Compare preceding abstract).—The mobility of the slowly-moving ions in the air is found to depend on the amount of moisture present. When the amount of moisture is altered to a considerable extent, an interval of several minutes elapses before the ions are in equilibrium with the new vapour-pressure conditions. H. M. D.

Ionisation in Various Gases. E. PARR METCALFE (*Phil. Mag.*, 1909, [vi], **18**, 878—889).—In order to ascertain whether the ionisation produced in different gases can be represented as the sum of the ionisations contributed by the atoms composing the molecules, experiments have been made on gases representing series of compounds containing the same two elements. The α-radiation from thin layers of uranium oxide was used as the ionising agent. The pressure of the different gases in the ionisation chamber was adjusted so that the stopping-power for the α-rays was approximately the same in every case.

For hydrogen, methane, ethane, propane, butane, and pentane, the relationship between the molecular ionisation and chemical composition is such that the addition of CH_2 to the molecule increases the molecular ionisation by an approximately constant amount, 0·92. Deducting 0·23 as the contribution of the two atoms of hydrogen, the value for carbon is found to be 0·69. This is very nearly the same as the value obtained for carbon from the series: methyl, ethyl, and butyl alcohols. On the other hand, the series oxygen, carbon dioxide, carbon monoxide yields for carbon the value 0·42. No simple additive relationship is evident in the series oxygen, nitric oxide, nitrous oxide.

From the results the conclusion is drawn that the contribution of an atom to the molecular ionisation is not constant, although for series of related compounds an additive law appears to be closely followed in some cases. H. M. D.

Chemical Reactions and the Ionisation of Gases. MAURICE DE BROGLIE and L. BRIZARD (*Compt. rend.*, 1909, **149**, 923—924).—Previous experiments of the authors have led them to the conclusion that the ionisation of a gas produced in a chemical reaction, or of a gas in which a reaction takes place, is not due to the chemical reaction itself, but to other causes (compare Abstr., 1909, ii, 637). Reboul (*ibid.*, ii, 718) has found, however, that air containing the fumes of ammonium chloride, formed by the combination of ammonia and hydrogen chloride, is ionised to a considerable extent; also that the

oxidation of a freshly-cut surface of sodium or of aluminium amalgam, or the formation of nitrous fumes, gives rise to conducting gases. The authors have repeated Reboul's experiments, taking great care to eliminate disturbing causes which would give rise to conduction, and find that under these conditions no gaseous ionisation takes place.

T. S. P.

Dielectric Constants of the Halogen Hydrides. OSCAR C. SCHAEFER and HERMAN SCHLUNDT (*J. Physical Chem.*, 1909, **13**, 669—672).—The dielectric constants of the liquid halogen hydrides were determined by Drude's method at two different temperatures with the following results: Hydrogen chloride, 4·60 and 8·85 at 27·7° and −90°; hydrogen bromide, 3·82 and 6·29 at 24·7° and −80°; hydrogen iodide, 2·90 and 2·88 at 21·7° and −50°. Solid hydrogen iodide gave 3·95 at −70°, and solid hydrogen cyanide, 2·4 and 3·05 at −25° and −70° respectively.

The low values of the dielectric constant are anomalous in view of the fact that the liquid halogen hydrides yield solutions of high conducting power when certain organic acids and alcohols are dissolved in them. The conclusion seems inevitable that other factors besides the dielectric constant must be considered in estimating the ionising power of solvents.

On solidification, hydrogen iodide shows an increase in dielectric capacity, whereas hydrogen cyanide shows a large decrease, the value for the liquid being about 100.

H. M. D.

Relation between Composition and Conductivity in Solutions of Meta- and Ortho-phosphoric Acids. EDMUND B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1909, **5**, 37—44).—The question as to what happens when vitreous meta-phosphoric acid or phosphoric oxide is dissolved in water has been studied by different investigators, and a review of the evidence shows that probably pyrophosphoric acid is not formed as an intermediate product. A consideration of the results of Sabatier (*Ann. Chim. Phys.*, 1899, [vi], **18**, 409) led the author to the conclusion that the process is mainly one of hydration, and it was thought that a study of the electrical conductivity of the changing solution would throw light on the subject.

The aqueous acid was prepared by adding pure phosphoric oxide to cold water, and contained 0·24 equivalent per litre. The amounts of meta- and ortho-phosphoric acids were determined from time to time by titration with alkali, using methyl-orange and phenylphthalein respectively as indicators; the electrical conductivity of the changing solution decreased at first slowly, then more rapidly, and then more slowly again. The solution when first made contains about 75% of the total dissolved acid as meta-phosphoric acid, the remainder being the ortho-acid; there is no evidence of the formation of pyrophosphoric acid. The metaphosphoric acid exists as both polymerised and simple molecules, the proportions of which may vary widely in different solutions of the same total concentration. The changes which take place in the solution are due to depolymerisation of the metaphosphoric acid, a process which is practically complete in twenty-four hours, and

hydration of the meta- to ortho-phosphoric acid. This last change takes place very slowly, not being complete in fourteen days at 25°.

T. S. P.

Effect of Temperature and Dilution on the Conductivity of Organic Acids in Aqueous Solution. GEORGE F. WHITE and HARRY C. JONES (*Amer. Chem. J.*, 1909, **42**, 520—541).—This investigation was undertaken in view of the fact that a systematic study of the conductivity and dissociation of organic acids with special reference to the effect of temperature and dilution has not hitherto been carried out. A brief review is given of previous work on conductivity and dissociation at various temperatures, and particularly that dealing with organic acids.

Jones and West (Abstr., 1905, ii, 794) and Jones and Jacobson (Abstr., 1908, ii, 1011) have shown that for a large number of substances between 0° and 35° dissociation decreases with rise of temperature, and Noyes (Abstr., 1904, ii, 226) has found that the same is true at high temperatures. It has also been stated by Jones and Jacobson (*loc. cit.*) that the molecular conductivity of electrolytes in aqueous solution increases as a parabolic function of the temperature, and this is explained on the hypothesis that all electrolytes in aqueous solution are more or less hydrated.

A study has been made of the conductivity of aqueous solutions of acetic, propionic, *n*-butyric, phenylacetic, malonic, succinic, *o*-phthalic, benzoic, salicylic, gallic, cinnamic, *o*- and *p*-aminobenzoic, and sulphanilic acids, the measurements being made at temperatures between 0° and 35°, and at dilutions ranging from $N/2$ to $N/2048$. The dissociation at 25° was calculated in each case by means of Ostwald's values for the conductivity at infinite dilution. The results are tabulated.

The dissociation constants of the dibasic acids, namely, malonic, succinic, and *o*-phthalic acids, increase considerably from the dilution $N/1024$ to that of $N/2048$, and it is therefore between these dilutions that the second hydrogen atom begins to dissociate.

The increase with dilution of the constants of *o*- and *p*-aminobenzoic acids is probably due to the breaking down of the inner salts on dilution.

The temperature-coefficients of nearly all the acids decrease regularly with dilution and rise of temperature, and are generally small and of the same order of magnitude; this is in accordance with the hydration theory. The viscosity of the medium is the chief factor which influences increase of conductivity of acids with rising temperature. Sulphanilic and *o*- and *p*-aminobenzoic acids differ from the other acids in having very large percentage temperature-coefficients which decrease with dilution. Moreover, the conductivities of sulphanilic and *o*-aminobenzoic acids are not parabolic functions of the temperature. The temperature-coefficients of these three acids, expressed in conductivity units, increase greatly with rise of temperature. These peculiarities are probably due to the fact that these three acids, having both basic and acidic groups, form internal salts which break down as

the temperature rises, and the free acids conduct more readily than the salts themselves. E. G.

Transport Number of Hydrochloric Acid. ERNST H. RIESENFELD and B. REINHOLD (*Zeitsch. physikal. Chem.*, 1909, **68**, 440—458).—The sources of error in the determination of transport numbers by Hittorf's method are discussed, and it is shown that for the attainment of an equal degree of accuracy with solutions of different concentration, the diameter of the transport apparatus must vary as the cube-root of the concentration. An improved form of transport apparatus is described, the special feature of which is that the anode and cathode compartments are bent several times; this arrangement has been found very efficient for diminishing alterations in the intermediate layers. The apparatus was of the same diameter throughout.

With this apparatus the transport number, n, of the anion in solutions of hydrochloric acid of intermediate concentration has been determined at 18° with the following results: $0{\cdot}977N$, $n = 0{\cdot}155$; $0{\cdot}452N$, $n = 0{\cdot}155$; $0{\cdot}104N$, $n = 0{\cdot}161$. G. S.

Determination of Transport Numbers from *E.M.F.* Measurements in Solvents which are only Partially Miscible with Water. ERNST H. RIESENFELD and B. REINHOLD (*Zeitsch. physikal. Chem.*, 1909, **68**, 459—470).—The *E.M.F.* of concentration cells, made up with two non-miscible solvents, is calculated for the general case when the concentration in the second solvent has any value whatever. In two cases: (1) when the concentration in the second solvent is small; (2) when the two solvents are in partition equilibrium, the *E.M.F.* of the cell is represented by the simple expression $E = RTn_2 \log C_1/C_2$ [1], where n_2 is the transport number of the anion of the binary electrolyte in the second solvent, and C_1 and C_2 are the concentrations of the electrolyte in the first solvent in contact with the anode and cathode respectively.

From measurements of the *E.M.F.* of cells of the second type, the transport numbers of the anions of potassium chloride and bromide in phenol as second solvent have been determined. Phenol was brought into partition equilibrium with $N/10$ (Phenol I) and $N/100$ (Phenol II) aqueous solutions of the electrolyte by shaking in a separating funnel for some time, and a cell of the following type: electrode | $N/10$ aqueous solution | Phenol I | Phenol II | $N/100$ aqueous solution | electrode, was then constructed and its *E.M.F.* measured. The electrodes were reversible with regard to the cation.

From the results, the transport number of the anions in phenol was calculated by equation [1], and both salts gave the same value, 0·439. A direct determination by Hittorf's method of the transport number of the anion in potassium chloride dissolved in phenol gave the value 0·475, which is probably less accurate than the above value.

For all the alkali salts examined, the relative velocity of the anion with reference to that of the cation is less in phenol than in water. G. S.

Relative Rates of Migration of Ions in Aqueous Solution. I. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1909, **5**, 165—171).—The transport numbers of the chlorides, bromides, and iodides of sodium, potassium, ammonium, rubidium, cæsium, magnesium, calcium, strontium, and barium have been determined by the method of direct observation of moving ionic boundaries, using the apparatus previously described by the author in conjunction with Steele (Abstr., 1906, ii, 68, 329). The concentrations of the solutions were 0·1 to 0·02 normal. The ionic mobilities in cm./sec. per volt./cm. are also calculated, together with the molecular conductivities. T. S. P.

Thermo-electric Forces of Certain Metallic Oxides and Sulphides. J. WEISS and J. KOENIGSBERGER (*Physikal. Zeitsch.*, 1909, **10**, 956—957).—The thermo-electric forces obtained by combination of certain oxides and sulphides with metallic copper have been measured. The temperatures of the hot and cold junctions, 80° and 20° respectively, were measured by small thermo-elements in direct contact with the junctions. Considerable care was taken to obtain perfectly homogeneous material for the experiments, for it is to the lack of homogeneity that the discrepant values obtained by previous observers are attributable. Values of the thermo-electric potential difference per 1° difference of temperature are recorded. H. M. D.

Very Short Electromagnetic Waves. Anomalous Reflexion and Dispersion of Liquids. H. MERCZYNG (*Compt. rend.*, 1909, **149**, 981—983).—Maxwell's relation, that the square of the refractive index is equal to the specific inductive capacity (dielectric constant), does not hold for many substances, especially for liquids. There should exist a region of transition between that where the index of refraction is defined optically and that where it is defined electrically for very long waves. Drude (Abstr., 1897, ii, 438, 537) used electrical waves of $\lambda = 75$ cm., and Cole of $\lambda = 5$ cm. The author uses waves of $\lambda = 4{\cdot}5$ cm., and determines the index of refraction (n) of a liquid by measuring the angle of incidence (i) of the rays and the ratio (R) between the intensities of the reflected and direct waves, making use of Fresnel's equation: $\sqrt{R} = (\sqrt{n^2 - \sin^2 i} - \cos i)/(\sqrt{n^2 - \sin^2 i} + \cos i)$. The dielectric constant (D) is then calculated from the refractive index, assuming that $D = n^2$. The results are as follows, and at the same time the dielectric constant (D_{opt}) calculated from the optical refractive index and that (D_{el}) calculated from the refractive index for long electrical waves are given for comparison:

Liquid.	D.	D_{opt}.	D_{el}.
Glycerol	16·8	2·1	56
Methyl alcohol	29·4	1·8	32—33
Amyl alcohol	3·31	1·9	16
Acetic acid	3·5	1·9	9·7
Aniline	4·36	2·5	7·4
Ethyl ether	3·26	1·9	4 25

T. S. P.

Conditions Necessary for Maintaining Platinum in a State of Incandescence in the Interior of a Bunsen Burner. JEAN MEUNIER (*Compt. rend.*, 1909, **149**, 924—926).—The author has

shown previously that the property which platinum possesses of remaining incandescent in a mixture of air and coal gas depends on the composition of the mixture (Abstr., 1909, ii, 311). He now shows that if a platinum wire is first cleaned with hydrochloric acid and then heated, it loses the property of remaining incandescent; if, however, it is passed between the fingers it regains that particular property because it takes up saline matter from them. This saline matter can be removed from the fingers by washing them in acidified distilled water, but not with soap and water.

Below a certain limit, the duration of the incandescence depends on the weight of substance deposited on the wire. From experiments with ordinary water containing 1·070 grams of total solids per litre, the relation between the duration of incandescence and the weight of substance deposited on the wire was determined. It was found, for example, that if the incandescence persisted for three minutes, the weight of substance deposited on the wire was 6/10,000 mg.

Thus platinum itself is not responsible for the incandescence, but rather the saline matter which is on its surface. T. S. P.

Theoretical Cooling Curves of Binary Mixtures. Étienne Rengade (*Compt. rend.*, 1909, **149**, 782—785).—The cooling curve of a pure substance consists of three practically straight lines, namely, the liquid cooling curve, the constant temperature during solidification, and the solid cooling curve. In the case of a mixture, the middle curve, that is, the cooling curve between the liquidus and the solidus, can be approximately calculated as follows. Assuming that A and B retain their specific heats unchanged in presence of each other, that the latent heat of solidification of A is unaffected by B in the mother liquor, and that the lowering of the freezing point of A is strictly proportional to the concentration of B, the author calculates that $\lambda dt = (1-s)[(1-C_1)m_1 + C_1m_2]dy + sm_1'dy + Lds$, where s molecules of A are deposited in time t, during which the freezing point falls by y° and the concentration of B increases from C to C_1; m_1, m_2 represent the specific heats of liquids A,B, and m_1' of solid A. This expression, simplified by assuming that m_1, m_2, and m_1' are all equal, yields on differentiating: $(m_1y - \lambda t + L)(Ky + C) = CL$.

The curve to this equation is an hyperbola having as asymptotes the lines $m_1y - \lambda t + L = 0$ and $Ky + C = 0$, the latter being parallel to the axis of t.

The cooling curve is a straight line to the point [0,0], where solidification begins with separation of A, and then follows the hyperbola. If $C = 0$, that is, if B is absent, the hyperbola reduces to its asymptotes, namely, a right line parallel to the axis of t during solidification and a right line representing the cooling of the solid A. Cooling curves determined experimentally in the author's automatic apparatus (Abstr., 1909, ii, 573) are in complete accord with the above analytical equations.

Other cases, where m_1, m_2, and m_1' are not equal, are also discussed.

R. J. C.

Theoretical Form of the Cooling Curves of Binary Mixtures The Case of Solid Solutions. ÉTIENNE RENGADE (*Compt. rend.*, 1909, **149**, 990—993).—Making use of the same assumptions as those employed in a previous paper (preceding abstract), the author deduces an equation for that part of the cooling curve of a binary mixture lying between the point of initial separation of the solid and the point of complete solidification, assuming that a solid solution is formed. The resulting curve is a hyperbola, one of the asymptotes being fixed and inclined to the time-axis, whereas the other asymptote is movable, but always parallel to the time-axis. A consideration of the curve shows that the point of complete solidification is always less marked than the point where the solid commences to separate. Other relations are also deduced which depend on the latent heats of fusion of the two components. T. S. P.

Superheating of Crystals. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1909, **68**, 257—269).—The paper contains a theoretical discussion of the conditions under which a crystal can be superheated while it is melting. Such superheating is always possible when the flow of heat to the crystal is sufficiently great, and can be realised the more easily the smaller the maximum linear velocity of crystallisation. It is, however, only during melting that crystals can be heated above the melting point.

These considerations have been tested by supplying heat to three substances of different crystallisation velocity, naphthalene, betol (β-naphthyl salicylate), and dextrose, and determining the rate of change of temperature with the time. For naphthalene there is a definite halt at the melting point, corresponding with the relatively great velocity of crystallisation, but for betol and dextrose, the velocity of crystallisation of which is slow, there is a rise of temperature during melting, so that the crystals of the latter two substances can be superheated.

The melting point of substances which do not melt sharply can in many cases be determined by a dilatometer method. The melting point of lævulose determined in this way is 91°, but the results are complicated by the fact that this substance undergoes some change when heated in the neighbourhood of its melting point.

It might be supposed that the extremely slow rate of crystallisation of many fused sugars is connected with molecular complexity, but molecular weight determinations by the cryoscopic method lend no support to this suggestion. G. S.

Melting-point Apparatus which can also be Used for the Determination of Solubilities with small Quantities of Substance. H. STOLTZENBERG (*Ber.*, 1909, **42**, 4322—4324).—Two new forms of apparatus are described, (*a*) for temperatures up to 350°, and (*b*) for low temperatures down to − 60°. The apparatus is similar in principle to Thiele's apparatus (Abstr., 1907, ii, 330), but the circulation is brought about, not only by heating or cooling a spiral side-tube, but also by bubbling carbon dioxide through it. For

solubility determinations, a sieve containing the solid is hung in the tube which contains the thermometer; owing to the rapid circulation of the liquid, a saturated solution is rapidly obtained. T. S. P.

Iodine as a Cryoscopic Solvent. F. OLIVARI (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 384—389).—The molecular depression of the freezing point of iodine, determined by means of arsenious iodide, lead iodide, stannic and mercuric iodides, has the mean value 213 (compare Timmermans, Abstr., 1906, ii, 429; Beckmann, Abstr., 1909, ii, 642); van't Hoff's equation gives the value 13·88 for the latent heat of fusion of iodine in place of the number, 11·7, employed by Timmermans.

Determination of the molecular weights in freezing iodine of a number of hydrocarbons, halogen derivatives, ketones, anhydrides, and acids, which can be separated unchanged by removing the iodine by means of thiosulphate, gives the following results: (1) in general, the molecular weights are greater than the theoretical numbers, and increase rapidly with the concentration; (2) this increase becomes more and more rapid on passing from the hydrocarbons towards the acids; (3) the molecular weights at infinite dilution, determined by extrapolation, approach the normal values for the hydrocarbons and their halogen derivatives, but are still greater, by varying amounts, than the theoretical numbers for succeeding compounds in the passage towards the acids.

These anomalous values are due to: (1) the fact that, owing to the high density of iodine (about 4), weight concentrations in proportion to the numbers 1, 2, 3, etc., correspond with volume concentrations in proportion to 4, 8, 12, etc., so that the concentrations rapidly attain values to which the fundamental cryoscopic laws are inapplicable; (2) the varying degree of polymerisation of the dissolved substance, and (3) the formation of additive, hydrate-like compounds of iodine with the liquid in which it is dissolved (compare Beckmann, Abstr., 1895, ii, 382; 1907, ii, 340; Vaubel, Abstr., 1901, ii, 446; Hantzsch and Vagt, Abstr., 1902, ii, 8; Lachmann, Abstr., 1903, ii, 283; Strömholm, Abstr., 1903, ii, 644; Hildebrand and Glascock, Abstr., 1909, ii, 225).

The molecular weight will be greater than the normal if the substance R forms a complex I_mR_n, in which n is greater than 1. If the complex dissociates according to the scheme: $I_mR_n \rightleftharpoons I_mR_{n-1} + R$, $I_mR_{n-1} \rightleftharpoons I_mR_{n-2} + R$, etc., increase of the concentration of R will favour equilibria corresponding with higher molecular weights (compare also Beckmann, Abstr., 1909, i, 652).

The molecular weight of tetramethylammonium iodide in freezing iodine is found to be 257·4—273 (200·9); of potassium iodide, 229·6—240·5 (166); of calcium iodide, 1043—1165 (293·8), and of strontium iodide, 900·6—1077 (341·34). Iodine solutions of sulphur containing 0·8951—2·36% of sulphur give molecular weights corresponding with S_8, more dilute solutions giving lower values (compare Abstr., 1909, ii, 37); these results are not in accord with the results of thermal analysis of mixtures of sulphur and iodine, which indicated partial isomorphism between the two elements (compare Ephraim, Abstr., 1908, ii, 581). The molecule of selenium in iodine solution is of

the order of magnitude Se_2 (compare Abstr., 1909, ii, 805). Tellurium combines directly with fused iodine; measurements made with a sample of 94% tellurium give the molecular weights 159—171·2 (Te = 127·6).

T. H. P.

Vapour Pressures at Low Temperature. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 365—373).—For measuring vapour pressures at low temperatures, the author employs an apparatus devised by Nernst, which was graduated by a manometer containing paraffin oil of known density. That the apparatus gives trustworthy results is shown by measurements of the vapour pressure of ice at the temperatures $-43·5°$, $-38·5°$, and $-30°$, the results obtained being in good agreement with those of Scheel and Heuse (Abstr., 1909, ii, 643), who employed a Rayleigh manometer.

For naphthalene, the vapour pressure is found to be 0·00878 mm. of mercury at 0°, and 0·0381 mm. at 15·0° (compare Allen, Trans., 1900, **77**, 400). The values calculated by means of Nernst's formula: $\log_{10} p = -\lambda_0 T/4·571 + 1·75 \log T - \epsilon T/4·571 + C$ (in which p indicates the vapour pressure in atmospheres at the absolute temperature T, and λ_0, ϵ, and C are constants) are 0·0083 mm. at 0° and 0·0396 mm. at 15°.

For iodobenzene, the values obtained are: 0·0189 mm. at $-25·8°$, 0·0310 mm. at $-19·8°$, 0·0701 mm. at $-11·5°$, and 0·0887 mm. at $-8·1°$. From the first of these values, that of Young (Trans., 1889, **55**, 486) for 160° and the value at 67·46° obtained by interpolation, the author calculates the constants of Nernst's formula (*vide supra*), and from the latter the vapour pressures at temperatures varying from $-25·8°$ to 200°, the calculated values being in good agreement with the author's and Young's results.

Similar calculations for bromobenzene give numbers in good accord with the experimental values of Young (*loc. cit.*) and the author, Nernst's formula being thus verified. The author's values are: 0·0956 mm. at $-26·1°$, 0·164 mm. at $-20·0°$, 0·186 mm. at $-18·5°$, and 0·191 mm. at $-17·7°$.

T. H. P.

Critical Phenomena of Solution. J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1909, **23**, 433—454. Compare Abstr., 1909, ii, 981).—From a consideration of the critical solution phenomena exhibited by different pairs of liquids, it is shown that these can be divided into three groups. The characteristics of one of these groups have been examined in detail with reference to the form of the critical solution curves on the pressure-temperature diagram. For a particular isothermal, three critical points may be realised as the pressure is gradually raised. This is a consequence of the retrogressive character of the pressure-temperature curve.

H. M. D.

Recent Investigations in Thermochemistry. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1909, **31**, 1275—1283).—An account of recent advances in the methods of thermochemical investigation.

E. G.

Alteration of Compressibility with the Softening of an Amorphous Substance. ALFRED DENNYS COWPER and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1909, **68**, 281—288).—A special form of apparatus for determining compressibilities is described and figured. It consists of a cylindrical vessel, in which the substance to be examined is placed; the vessel is connected on one side with a manometer and on the other with a steel cylinder, in which a well-fitting ebonite piston moves. The distance through which the piston has to be moved in order to alter the pressure from p_1 to p_2 is measured, and from this and the constants of the apparatus the compressibility is calculated.

In practice, it is only for such viscous liquids as castor oil that the filtration past the piston does not cause serious error at high pressures, and measurements have therefore been made with castor oil alone, and when part of the oil is displaced by crystalline and by amorphous dextrose respectively. The coefficients of compressibility of castor oil, at temperatures from 25° to 100°, and at pressures of 250—2000 kilog./cm.^{2}, are given in tabular form, and the coefficients for crystalline and amorphous dextrose are given between the same limits. Between 25° and 100° and from 250—1500 kilog.-pressure, the coefficient of compressibility of crystalline dextrose is independent of temperature and pressure, and is 76×10^{-7} when referred to the volume at 25° and 1 kilog.-pressure. The compressibility of amorphous dextrose is about double that of the crystalline form; it increases somewhat with increasing temperature, and diminishes with increasing pressure. G. S.

Connexion of Surface-tension with the Internal Pressure and van der Waals' Constants *a* and *b*. ISIDOR TRAUBE (*Zeitsch. physikal. Chem.*, 1909, **68**, 289—294).—In connexion with Walden's series of papers on the same subject (compare Abstr., 1909, ii, 119, 123, 547), the author maintains his priority in some points, and supplements his own and Walden's work by further values of *a* and *b* and of internal pressures. The results show that the ratio of *a* to *b* is approximately the same for all substances, and, further, that the sum of the square roots of the atomic weights is proportional to the sum of the atomic volumes. G. S.

Viscosity of Water. RICHARD HOSKING (*J. Roy. Soc., New South Wales*, 1908, **42**, 34—56; **43**, 34—38).—In earlier measurements (compare Abstr., 1900, ii, 336) of the viscosity of water by the efflux method, the rate of flow of liquid in the capillary tube was made so small that the kinetic energy correction was of relatively small magnitude. New experiments have been made in which the rate of flow was increased, with the object of testing the formula by means of which correction was made for the kinetic energy. As the pressure determining the flow is increased, there appears to be an abrupt change in the numerical factor contained in the kinetic energy reduction term, or a change in the nature of the flow. Consistent values for the viscosity at 50° were, however, obtained, until the kinetic energy correction was as high as 60%. The absolute values of the viscosity

of water at 0°, 25°, and 50° are 0·01793, 0·00893, and 0 00550 respectively. It is estimated that the probable error of these values is only 0·1%.

The measurements of the viscosity were extended up to 100°. Values representing the viscosities and the relative fluidities are tabulated for every 5° between 0° and 100°. For temperature intervals of 25° the viscosity data can be accurately represented by formulæ of the type $\eta_t = \eta_0/(1 + k_1t + k_2t^2)$. A less exact representation over the whole range of temperature is afforded by the formula

$$\eta_t = 9{\cdot}185/(46{\cdot}694 + t) \times 1{\cdot}6232.$$

H. M. D.

Viscosity of Solids at Low Temperatures. CHARLES E. GUYE and V. FREEDERICKSZ (*Compt. rend.*, 1909, **149**, 1066—1069).—Guye and Mintz have investigated previously the effect of rise of temperature on the viscosities of certain metals (Abstr., 1908, ii, 930), and this work has now been extended to the investigation of the effect of lowering of temperature.

Silver, aluminium, iron, gold, magnesium, and quartz were each examined at 100°, 50°, 0°, −80°, and −196°. The first three showed decreases in viscosity with lowering temperature, but probably the viscosity does not become zero at −273°. Magnesium and gold show decreases in viscosity until −80° is reached, but at −196° exhibit a considerable increase. The modulus of elasticity augments with fall in temperature for the metals, but the reverse is the case with quartz.

T. A. H.

Mechanism of the Adsorption ("Sorption") of Hydrogen by Carbon. JAMES W. McBAIN (*Phil. Mag.*, 1909, [vi], **18**, 916—935; *Zeitsch. physikal. Chem.*, 1909, **68**, 471—497).—Experiments have been made on the adsorption of hydrogen by cocoa-nut charcoal at the temperature of liquid air, which show that the process is of dual character, consisting in a surface condensation and the formation of a solid solution accompanied by diffusion into the interior of the carbon.

By suitable manipulation a sample of carbon can be prepared which contains a considerable amount of hydrogen in a state of solid solution, but is almost destitute of hydrogen condensed on the surface. This condition is attained by suddenly exposing to low pressure carbon which has been previously saturated by long contact with hydrogen.

The fact that the surface condensation is nearly instantaneous, whereas the diffusion process requires several hours, enables the two phenomena to be separately examined, and various methods for the isolation of the two effects are described.

The true solubility (as distinguished from the surface condensation) of hydrogen in cocoa-nut carbon at the temperature of liquid air varies with the square root of the pressure, indicating that the dissolved hydrogen is split up into simple atoms. The solubility amounts to 4 c.c. (corr.) of hydrogen per gram of carbon when the pressure is 19 mm. of mercury. The true solubility at the ordinary temperature is less than one hundredth as great.

The term "sorption" is suggested to embrace all adsorption and occlusion phenomena.

H. M. D.

Relations between the Critical Constants and Certain Quantities connected with Capillarity. R. D. KLEEMAN (*Phil. Mag.*, 1909, [vi], 18, 901—908. Compare Abstr., 1909, ii, 645, 869).—A further relationship between the pressure, density, and molecular weight of liquid substances is deduced. This is found to be satisfied by a large number of organic compounds, but not by water or ethyl alcohol, and the abnormal behaviour of these is attributed to molecular association. H. M. D.

Kinetic Interpretation of Osmotic Pressure. M. M. GARVER (*J. Physical Chem.*, 1909, 13, 679—690).—A hypothesis is put forward to explain the general properties of solutions. The addition of a foreign non-volatile substance to a pure solvent is supposed to have the effect of narrowing the range of the velocities of the molecules of the solvent.

Although therefore the average molecular energy of translation will depend on the absolute temperature, there will be a smaller proportion of molecules which have exceptionally high or low velocities in a solution as compared with the proportion in the pure solvent. On the basis of this hypothesis, the depressed vapour tension of solutions and the phenomena of isothermal distillation, osmosis, and diffusion can be easily interpreted.

The osmotic transport of the solvent through a semipermeable membrane can be explained equally readily whether it be assumed that the interstices of the diaphragm are occupied only by the vapour of the solvent or that the solvent actually penetrates and comes into contact with the solution on the further side of the membrane. H. M. D

Osmotic Pressure of Colloids. I. Function of Electrolytes in the Dialysis of Colloids. WILHELM BILTZ and ARVED VON VEGESACK (*Zeitsch. physikal. Chem.*, 1909, 68, 357—382).—A special form of osmometer is described, in which the membrane consists of a collodion film deposited on a perforated frame of platinum. The upper part of the arrangement is a glass vessel, which is firmly fixed below to the platinum frame, and is provided with a narrow side-tube, which acts as a manometer. Through the upper part of the glass vessel passes a stirrer, driven by an electro-magnet. There are also arrangements by which the electrical conductivity of the solutions outside and inside the cell can be measured. The whole arrangement was placed in a thermostat at 25°. Measurements were made with benzopurpurine, night-blue, ferric and zirconium hydroxides, and tungstic acid. The general result of the observations was that in no case were equilibrium pressures obtained.

A solution of benzopurpurine was dialysed twenty days to free it, as far as possible, from electrolytes, and then placed in the osmometer. After six hours, the osmotic pressure was 10 mm. of water; after ten hours, 10·66 mm., and then it gradually diminished, until in twelve days it had fallen practically to zero. It was observed that immediately after the stirrer was started, the pressure always rose a little, and this is ascribed to the mixing of the solution in the upper glass

part of the manometer with the lower part, which had gradually become poorer in electrolytes by diffusion through the membrane When sodium sulphate is added in equivalent amount to both outer and inner liquid, the osmotic pressure is very slight. Further, when undialysed benzopurpurine is used in the osmometer, and a little sodium sulphate is added to the outer water, in course of time the conductivity becomes equal outside and inside, and there is practically no osmotic pressure. The other colloids gave similar results.

The gradual fall in the osmotic pressure is due mainly to dialysis of the electrolyte, but partly also to a gradual increase in the size of the colloidal particles. This explanation has been confirmed by experiments with dilute solutions of sodium sulphate and of night-blue respectively. In the latter case, in the absence of stirring, a false equilibrium was obtained, the tendency to rise being balanced by the dialysis of the electrolyte.

Better results should be obtained by using the filtrate from the colloidal solution as outer liquid (Duclaux), but it is not certain that the former represents the unaltered intermicellar liquid. G. S.

Influence of Substances in Solution on the Velocity of Crystallisation and the Crystal-habit of Potassium Sulphate. W. Wenk (*Zeitsch. Kryst. Min.*, 1909, **47**, 124—162).—Inorganic salts (various salts of potassium and sodium), added to a solution of potassium sulphate, exert a marked influence on the velocity of crystallisation of the latter salt, the growth being increased in some cases and retarded in others. Since the viscosity of the solution is not affected by these additions, it follows that the velocity of crystallisation is not dependent on diffusion; and it appears to be rather connected with adsorption and surface-tension. Organic colouring matters in the solution have a still more marked influence on the velocity of crystallisation, and they further produce an alteration in the habit of the crystals, and the colouring matter is adsorbed. L. J. S.

Isomerism and Polymorphism. Andreas Fock (*Ber.*, 1909, **43**, 4527—4531).—The different crystal forms of polymorphic modifications are attributed to external and internal influences. The former include pressure, temperature and volume, and it is well known that the range of existence of the various polymorphic forms is sharply bounded by these factors. The internal influences are afforded by the configuration of the molecule, including the arrangement, position, and motion of the atoms. Alteration in pressure or temperature brings about an alteration in configuration. In solids these parallel changes are not continuous, but take place in jerks; in liquids and solutions probably both changes are continuous. In the case of an amorphous solidification, all the various configurations of the molecule present remain intact. In the various cinnamic acids, it is suggested that a slight difference in the chemical molecule is, to some extent, associated with the isomerism. E. F. A.

Preparation of Colloidal Solutions by the Disintegration of Metals by Ultra-violet Light. The Svedberg (*Ber.*, 1909, **42**, 4375—4377).—The metal, from which the colloidal solution is to be

formed and the surface of which has been freed from oxide, is placed in a flat dish, covered with the dispersion medium, and submitted to the action of the ultra-violet light from a Heraeus quartz mercury lamp placed a few centimetres above the liquid. After a few minutes the latter, when examined in the ultramicroscope, shows the characteristic properties of a colloidal solution.

Silver, copper, tin, and lead readily give colloidal solutions in this way, whereas platinum, aluminium, and cadmium do not. With water as the dispersion medium, lead gives a milky liquid, probably containing colloidal lead hydroxide, in five minutes; with alcohol in the place of water, a colloidal metal solution is obtained in the same time. Experiments with lead and silver in water, ethyl alcohol, *iso*butyl alcohol, ethyl ether, acetone, ethyl acetate, and amyl acetate showed that the number and size of the colloidal particles may vary very much, and that the disintegration depends on the nature of the dispersion medium. It was possible to produce sols which contained very small particles of very uniform size, these particles being in brisk Brownian movement. T. S. P.

Phase Rule. JOSEPH A. MULLER (*Compt. rend.*, 1909, **149**, 1079—1080).—A reply to Boulouch (Abstr., 1909, ii, 802) maintaining the validity of the author's method of deducing the relationship between the number of substances and phases of a system in equilibrium (Abstr., 1908, ii, 466). T. A. H.

Photo- and Electro-chemical Equilibria. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 356—359).—From a consideration of the equilibria in systems which are capable of absorbing light energy and electrical energy, the author is led to the view that equilibria will be established at the ordinary temperature which correspond with higher temperatures in the absence of these other forms of energy. In this connexion, reference is made to the special cases of the dissociation of hydrogen sulphide, hydrogen selenide, hydrogen iodide, the hydrides of phosphorus, arsenic, and antimony, and also of carbon dioxide. H. M. D.

Temperature-coefficient of Chemical Reaction Velocities. IV. The Velocity Isochore of Gas Reactions, its Connexion with that of the Reactions of Free Atoms, with Applications. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, **68**, 295—315. Compare Abstr., 1909, ii, 651).—A theoretical paper. A general equation, independent of the validity of the gas laws for the vapours of the reacting substances, is deduced for the velocity of gas reactions. Contrary to the former method of deduction, the heat developed in the reaction is partitioned out according to the intermediate reactions to be assumed on chemical grounds, and Nernst's thermodynamic law is employed. The equation is applied to the experimental data for the influence of temperature on the decomposition and formation of hydrogen iodide, and on the decomposition of nitric oxide and of hydrogen phosphide, and is shown to be in satisfactory accordance with the results. G. S.

Rate of Evolution of Gases from Homogeneous Liquids. VICTOR H. VELEY (in part, with JOHN C. CAIN) (*Trans. Faraday Soc.*, 1909, **5**, 1—9. Compare Trans., 1883, **43**, 370; 1903, **83**, 736; Abstr., 1903, ii, 641, etc.).—Utilising the results previously obtained by himself and other workers, the author has studied the conditions of the evolution of gases from liquids in which chemical changes are taking place, with especial reference to the degree of supersaturation, which, according to the author, appears to have been greatly over-estimated. The reactions considered are: (1) carbon monoxide from formic and sulphuric acids, (2) nitrogen from ammonium nitrite, (3) oxygen from hydrogen peroxide solutions, and (4) nitrogen from the decomposition of diazonium salts by water.

The amounts of gases retained in supersaturated solution are calculated by comparing the volumes which were actually evolved and those which would have been obtained if there had been no retention (compare Abstr., 1903, ii, 641). From the known solubilities of the several gases in water, the degree of supersaturation can then be determined. The values obtained vary between 8 and 12, according to the nature of the gas and the conditions of experiment.

In a few cases of the decomposition of diazonium salts, the lag factors due to certain opposing side reactions are discussed, and their effects separated from the concomitant initial delay due to gas retention. T. S. P.

Hydrolysis and Reaction Velocity in Mixtures of Alcohol and Water. HANS EULER and BETH AF UGGLAS (*Zeitsch. physikal. Chem.*, 1909, **68**, 498—510).—The degree of ionisation and of hydrolysis of certain compounds in 80 per cent. alcohol has been determined by conductivity measurements. The dissociation constants $k \times 10^5$ for salicylic acid are as follows: 1·81 at 0°, 1·86 at 18°, 1·88 at 30°, the values being about 1/50 of those in aqueous solution. As regards the hydrolysis of aniline salicylate, the non-hydrolysed fraction in $N/10$ solution is 0·73 at 0°, 0·57 at 18°, and 0·51 at 30°. From this the dissociation constant of aniline at 18° is estimated at $k = 4 \times 10^{-12}$, assuming that the ion-product for the solvent is $0·6 \times 10^{-16}$. In $N/100$ solution the sodium salt of benzaldehyde is practically completely hydrolysed, the corresponding salt of *p*-nitrobenzaldehyde to the extent of 76%, and the corresponding salt of dextrose to 47%. The latter is thus less hydrolysed in 80 per cent. alcohol than in pure water.

An attempt was made to follow the rate of neutralisation of aniline by salicylic acid at −50° by the conductivity method, but the reaction is complete within ten seconds.

Electrical conductivity measurements indicate that phenolphthalein is a dibasic acid, and this conclusion is supported by colorimetric measurements. The red colour of concentrated alcoholic solutions of phenolphthalein salts is intensified by raising and diminished by lowering the temperature. G. S.

Hydrolysis of Salts of Amphoteric Electrolytes. HEATHER HENDERSON BEVERIDGE (*Proc. Roy. Soc. Edin.*, 1909, **29**, 648—667).—The results obtained for the degree of hydrolysis of amphoteric

electrolytes by the methods depending on the measurement of the rate of catalysis of methyl acetate and that of the electrical conductivity are not in agreement. With the object of throwing light on this discrepancy, the hydrolysis of *o*-aminobenzoic acid in acid solution has been determined by these and other methods. It is found that those methods of determining the hydrolysis which depend directly on the concentration of the hydrogen ion agree fairly well with each other. Such methods examined were the catalysis of methyl acetate by the hydrochloride, and of ethyl diazoacetate by the nitrate, and the difference of potential method. Other methods involving the solubility of the amphoteric base in acid solutions of different concentrations and the partition of the base between two immiscible solvents lead to the same value. On the other hand, the more indirect methods depending on electrical conductivity and freezing-point measurements lead to different values for the degree of hydrolysis. The conclusion is drawn that these two methods cannot be used to determine the extent of hydrolytic decomposition in the case of salts of amphoteric electrolytes. The interpretation of the freezing-point and conductivity data leads to the view that there are fewer molecules in the solution of a salt of an amphoteric electrolyte than there would be in the case of a non-amphoteric substance. H. M. D.

Atomic Weights as Mathematical Functions. F. H. LORING (*Chem. News*, 1909, **100**, 281—286).—In continuation of previous work (compare Abstr., 1909, ii, 392) the elements are arranged in the order of their atomic weights according to a method already described, and the meaning of the gaps in the arrangement is further discussed. Nitrogen does not fit into the system, and it is suggested that it is made up of helium and two other unknown inactive elements, the so-called "satellite," St, atomic weight 0·27, and an element, Nt, atomic weight 9·75. The "satellite" may occur along with other elements, for example, iodine + 2 satellites = tellurium.

A further arrangement of the elements is given, the vertical columns in the table mentioned above, or the elements singly, are displaced downwards as required in order to bring chemically allied elements into horizontal alignment. If then the squares are coloured blue, red, or purple, according as the elements are basic, acidic, or neutral in character, the basic elements occupy a triangular area, the acidic ones next to them a similar area, and the elements of neutral tendency form a rectangle. Finally, where the acidic elements repeat, an approximate square is formed. A coloured table to illustrate this arrangement accompanies the paper. G. S.

Calculation of Atomic Weights. Solution of the Equation of Condition. GUSTAV D. HINRICHS (*Compt. rend.*, 1909, **149**, 1074—1076).—A graphic method of solution is described, which includes and generalises those already given (Abstr., 1907, ii, 945; 1909 ii, 653). The graph used in illustration of the method is that for 42 determinations of the ratio AgCl : Ag, commencing with Berzelius' first determination and ending with those of Richards (compare Abstr., 1907, ii, 679). T. A. H.

Molecular Rearrangements. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1909, 31, 1368—1374).—A discussion of recent conceptions with regard to molecular rearrangements, and particularly with reference to the nature of the forces or attractions which hold atoms together in molecules, and which also cause atoms of different molecules to react with each other. E. G.

Inorganic Chemistry.

Anodic Formation of Hydrogen Peroxide. FRANZ RICHARZ (*Ber.*, 1909, **42**, 4674—4675. Compare Riesenfeld and Reinhold, Abstr., 1909, ii, 879).—The secondary formation of hydrogen peroxide at the anode has been observed by the author (Abstr., 1885, 624; 1888, 12, 769). C. H. D.

Dissociation of Hydrogen Bromide and Hydrogen Iodide at High Temperatures. KURT VOGEL VON FALCKENSTEIN (*Zeitsch. physikal. Chem.*, 1909, **68**, 270—280).—The measurements were made by determining the partial pressure of the hydrogen by Lowenstein's method (compare Abstr., 1906, ii, 272). The dissociation of hydrogen bromide is 0·50% at 1024°, 0·73% at 1108°, and 1·08% at 1222°; that of hydrogen iodide is 32·9% at 1022° and 37·55% at 1217°. The results, and also the fact that at the high temperatures used the halogen molecules are partly dissociated according to the equations $Br_2 \rightleftharpoons 2Br^{\cdot}$ and $I_2 \rightleftharpoons 2I$, will be discussed in a later communication G. S.

Electric Conductivity and Density of Solutions of Hydrogen Fluoride. ERNEST G. HILL and ANNODA P. SIRKAR (*Proc. Roy. Soc.*, 1909, *A*, **83**, 130—148).—Measurements have been made of the electrical conductivity and density of mixtures of water and hydrogen fluoride ranging from the one pure substance to the other. A satisfactory conductivity cell was constructed from paraffin wax of low melting point (40·4°). The density measurements were made by weighing a lead cylinder coated with paraffin wax in the various liquids.

Curves are plotted which show the variation of the specific conductivity and of the density with the percentage composition of the solutions. These are of approximately the same type, and exhibit a well-defined maximum for a solution containing 75% of hydrogen fluoride. The curve, which is obtained when the molecular conductivity of the hydrogen fluoride is plotted as a function of the concentration, shows two distinct breaks, one at about 91%, the other between 51% and 55% of hydrogen fluoride. The former corresponds with the composition $9HF,H_2O$, the latter with HF,H_2O, and the

authors draw the conclusion that definite hydrates of this composition are present in the solutions.

From values obtained for the conductivity at 0° and 18°, the temperature-coefficient has been calculated. This is constant, and equal to 0·0125 for solutions containing less than 7·7% of hydrogen fluoride. By applying this temperature correction, molecular conductivity data for 25° are obtained. On comparison with Ostwald's numbers for dilute solutions, a satisfactory agreement is obtained at the dilution $v=4$, but for more dilute solutions the authors' numbers are much smaller than Ostwald's, the difference increasing with the dilution.

H. M. D.

Production of Ozone by Ultra-violet Light. EDMOND VAN AUBEL (*Compt. rend.*, 1909, **149**, 983—985).—Bordier and Nogier (*Compt. rend.*, 1908, **147**, 354) could not find that ozone was produced from the oxygen of the air by the action of ultra-violet light, although previous observers (compare Abstr., 1906, ii, 224; 1909, ii, 657) had observed its formation. Using a quartz mercury lamp as the source of ultra-violet light, the author definitely proves that ozone is produced. Instead of using water to absorb the ozone, olive oil and light petroleum were employed in the first experiments, being placed in porcelain dishes inside the large glass globe surrounding the quartz tube. After several hours' exposure, starch iodide showed the presence of ozone in these liquids. When distilled water was submitted to the action of the ultra-violet light for fourteen hours, the presence of ozone was detected by its action on a photographic plate. Starch iodide paper was turned blue in two minutes, except where it was covered with a piece of quartz, and thus prevented from coming into direct contact with the ozonised air.

T. S. P.

Boiling Point of Sulphur Corrected by Reference to New Observations on the Absolute Expansion of Mercury. HUGH L. CALLENDAR and HERBERT MOSS (*Proc. Roy. Soc.*, 1909, *A*, **83**, 106—108).—As a result of new measurements of the expansion of mercury between 0° and 300°, it has been found necessary to add a correction factor to the result obtained for the boiling point of sulphur by Eumorfopoulos (Abstr., 1908, ii, 1029). This raises the temperature from 443·58° to 444·55°, which is in practically perfect agreement with the value previously assumed (444·53°).

H. M. D.

The Dynamic Allotropy of Selenium. HUGO R. KRUYT (*Zeitsch. anorg. Chem.*, 1909, **64**, 305—326).—The study of the electrical conductivity is uncertain as a means of investigating the dynamic allotropy of selenium, conductivity not being an additive property. The author has, therefore, used the specific gravity, the reciprocal of which is a strictly additive property of solid solutions. The material was purified as described by Marc in his study of selenium (Abstr., 1904, ii, 105; 1906, ii, 226, 280, 742; 1907, ii, 453).

Grey, crystalline selenium, which has not been heated above 120°, has D 4·5—4·6, whilst sublimed selenium has D 4·80. The difference is not due to the presence of amorphous selenium. After fusion, passage

of the amorphous into the crystalline form, and heating to 125°, the preparation has D 4·77. The denser form passes into a modification with D 4·77 when heated to 125°. There is thus an equilibrium, $Se_A \rightleftarrows Se_B$, high temperatures favouring the denser form. Exposure to the light of an arc lamp, or even to bright diffused light, the selenium being enclosed in a dilatometer with alcohol, produces an increase of volume; the quantity of Se_A is, therefore, increased by illumination. The changes in the electrical conductivity are explained on the assumption that Se_A and Se_B form solid solutions, and also form a compound giving a diagram of the same form as is obtained from mixtures of bromine and iodine (Terwogt, Abstr., 1906, ii, 15) and alloys of magnesium and cadmium (Grube, Abstr., 1906, ii, 355). The conductivity has then two minima, with a sharp cusp on the curve corresponding with the compound. The anomalous behaviour of specimens cooled from 200° is explained as being due to the combined action of light and heat in altering the equilibrium, and also in changing the velocity with which equilibrium is attained.

The conclusion is drawn that all phases of selenium contain Se_A and Se_B, whilst red, crystalline selenium is labile, and may perhaps also occur in two modifications. C. H. D.

Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-Water, and of Atmospheric Carbon Dioxide in Sea-Water. CHARLES J. J. FOX (*Trans. Faraday Soc.*, 1909, 5, 68—86).—The apparatus used for determining the coefficients of absorption of nitrogen and oxygen was a modified form of Estreicher's adaptation (Abstr., 1900, ii, 205) of Ostwald's apparatus. The pressure used could be varied at will, whereas Estreicher's had to make the measurements at exactly atmospheric pressure. Special precautions were taken to free the water from dissolved air, and it is suggested that the method used by Estreicher was not satisfactory, so that his values for the absorption coefficients for argon and helium may be respectively 0·2 to 5% and 0·5 to 10% too low.

Two series of measurements of the solubility of atmospheric nitrogen in distilled water between 0° and 50° were made. A correction had to be applied, due to the different solubilities of nitrogen and argon and the variation of the partial pressures with temperature. The relation between the absorption coefficient (α_N) and the temperature is given by the formula $1000\alpha_N = 22{\cdot}998 - 0{\cdot}5298t + 0{\cdot}0091962t^2 - 0{\cdot}00006779t^3$. In the case of oxygen the formula obtained was $1000\alpha = 49{\cdot}239 - 1{\cdot}3440t + 0{\cdot}28752t^2 - 0{\cdot}0003024t^3$. These formulæ give the following values for gas absorbed in c.c. per litre.

	0°	10°	20°	30°	40°	50°
Nitrogen...	23·00	18·54	15·54	13·55	12·15	11·02
Oxygen ...	49·24	38·37	31·44	26·65	23·30	20·95

Determinations were also made on sea-waters of four different salinities. These values were then combined with those obtained for distilled water, and formulæ obtained connecting the absorption coefficient, temperature, and salinity (chlorine-content) of the sea-water for nitrogen and oxygen at the partial pressures they have in air.

Tables are then given showing the amount of nitrogen (containing argon) and oxygen (in c.c.) absorbed by 1000 c.c. of sea-water from a free dry atmosphere of 760 mm. pressure at temperatures from 0° to 28°, and the chlorine content 0—20 per mille.

In the case of carbon dioxide the pressure in sea-water varies probably between 1 and 7 parts per 10,000; the total alkalinity also varies, and for the open ocean is equivalent to about 40 mg. OH per litre. The carbon dioxide pressure was determined by a modification of Pettenkofer's method. It was first of all established that the ratio of total CO_2 to total OH is rectilinear, and as a result of the law of mass action no CO_3''-ions are formed; all the combined carbon dioxide must be in the form of HCO_3'. The effect of varying pressure on only one alkalinity, that selected being 40 mg. OH per litre, was then determined. From these results an interpolation formula connecting the carbon dioxide per litre of sea-water, the salinity, the alkalinity, the temperature, and the pressure was obtained, and tables of the calculated results are given.

From these tables a calculation can be made of the power of the sea to conserve the constancy of carbon dioxide in the air (compare Arrhenius, *Phil. Mag.*, 1896, [v], **41**, 273). The conclusion is drawn that for the open ocean (OH = 40 mg. per litre and $t = 12°$) it requires 17·6 times as much carbon dioxide to raise the carbon dioxide partial pressure as for the same volume of air; or, if a quantity of carbon dioxide is poured into the air, as, for example, by volcanic action, two-thirds will eventually be absorbed by the sea. The final equilibrium will not be attained, however, until either the insoluble carbonates on the sea-bottom or the carbon dioxide in the air have completely gone into solution in the form of HCO_3'. The time necessary for this is not known, but it must be very important geologically.

The concentrations of the free ions, HCO_3' and $H^{\cdot}$, for ocean-water are calculated to be respectively $2{\cdot}24 \times 10^{-3}$ and $1{\cdot}6 - 2{\cdot}6 \times 10^{-6}$ gram-equivalents per litre; thus sea-water is just slightly more acid that distilled water.

The paper also contains a description of the apparatus used for extracting and analysing gases dissolved in liquids.

T. S. P.

Red Phosphorus and the so-called "Hittorf's Phosphorus." Alfred Stock and Franz Gomolka (*Ber.*, 1909, **42**, 4510—4527).—Hittorf's phosphorus, having the high density 2·3, is the only variety, other than yellow phosphorus, which is at all well defined, the ordinary red variety being a mixture.

Hittorf's phosphorus is best prepared by heating 3 grams of pure phosphorus with 200 grams of lead in a sealed Jena glass tube, packed in sand, to 800° for forty-eight hours. The glass is broken and removed in a freezing mixture, and the lead cleaned by brushing and by washing with hydrofluoric acid. As nitric acid attacks the phosphorus, the lead is best removed by electrolysis in acetic acid containing lead. The cathode is placed at the bottom of the vessel, a clock-glass being fixed below the rod. The residue thus obtained contains some lead, mechanically dislodged from the anode, and is purified by boiling with

hydrochloric acid in an atmosphere of carbon dioxide, followed by treatment with hydrofluoric acid. The purest product still contains 1·5% of lead.

Bismuth may be used in place of lead, but it dissolves only one-fifth as much phosphorus, and the crystals obtained are less pure. The metals appear to be held in solid solution.

Only very minute quantities of Hittorf's phosphorus are obtained by sublimation. An improvement of this method is being studied.

Ordinary red phosphorus melts at 605—610°, and Hittorf's phosphorus at 620°. The product obtained by fusion in a closed tube is heterogeneous.

Hittorf's phosphorus, corrected for the dissolved lead, has D 2 31—2 33. It is much less chemically reactive than ordinary red phosphorus at high temperatures, but both oxidise slowly in the air to deliquescent products. The statement, often made, that red phosphorus is stable in air, is incorrect. C. H. D.

Oxidation of Phosphorus. WILLEM P. JORISSEN and N. H. SIEWERTSZ VAN REESEMA (*Chem. Weekblad*, 1909, **6**, 931—938. Compare Schmidt, Abstr., 1902, ii, 237; Schenck, Mihr, and Banthien, Abstr., 1906, ii, 326; de Broglie and Brizard, Abstr., 1909, ii, 535; Riboul, *ibid.*, ii, 718; Elster and Geitel, *Physikal. Zeitsch.*, 1902, **3**, 475; 1903, **4**, 111, 293, 436, 457; *Ber. deut. physikal. Ges.*, 1906, 640).—The work of Elster and Geitel and of Schmidt on the oxidation of phosphorus has been repeated. The results obtained support the conclusions of Elster and Geitel, but indicate that Schmidt's statements are erroneous. A. J. W.

Preparation of Hypophosphoric Acid. JACQUES CAVALIER and E. CORNEC (*Bull. Soc. chim.*, 1909, [iv], **5**, 1058—1060).—A number of glass rods are placed across the bottom of an ordinary photographic washing dish, and on these are laid transversely, sticks of phosphorus, separated from each other by glass rods. Water is then poured into the dish until the phosphorus is half submerged. The whole is covered by a glass plate resting on a layer of cotton wadding, so that air is slowly but continuously admitted. The acid formed can be neutralised by sodium carbonate, to form sodium hydrogen hypophosphate, or the latter salt can be obtained at once by substituting a solution of sodium acetate for water in the dish. From this sodium salt, the acid is best recovered by making the lead salt by double decomposition, and regenerating the acid with hydrogen sulphide. By this process, and using a dish 13 × 18 cm., from 30 to 50 grams of sodium hydrogen hypophosphate may be obtained in five to six days. T. A. H.

Decomposition of Water by Hypophosphites in Presence of Palladium as a Catalyst. ALEXIS BACH (*Ber.*, 1909, **42**, 4463—4470).—The formation of copper hydride from sodium hypophosphite and copper sulphate takes place at the ordinary temperature, and is an example of the decomposition of water by an oxidisable substance in presence of a substance capable of combining with hydrogen. The same reaction takes place in presence of a catalyst, hydrogen being set free.

Solutions of sodium hypophosphite and palladium chloride are used, the course of the reaction being followed by measuring the volume of hydrogen evolved. The velocity of decomposition increases much more rapidly than the quantity of palladium added, the concentration of the hypophosphite being kept constant. The velocity decreases rapidly with time, and is not increased by further additions of palladium, but rises to the original value on further addition of hypophosphite. With constant palladium, the velocity increases less rapidly than the quantity of added hypophosphite. Hydrocyanic acid prevents the decomposition, or, if palladium sponge is used instead of the chloride, slowly brings it to a standstill.

The analogy of the behaviour of palladium in this case to that of a peroxydase is pointed out, both departing from the laws of chemical kinetics. The intermediate formation of an unstable palladium perhydride is assumed. C. H. D.

Phosphorescent Oxidation of Arsenic. LÉON BLOCH (*Compt. rend.*, 1909, **149**, 775—777. Compare Abstr., 1909, ii, 395).—The phosphorescence of arsenic at 200°, like that of sulphur and phosphorus, is accompanied by oxidation, by which arsenic trioxide is produced. As in the case of sulphur, no ionisation occurs, and there is also no formation of ozone, which is produced by both sulphur and phosphorus. The product of oxidation of arsenic, either phosphorescently or with flame, always contains arsenic oxide, just as some phosphoric oxide and sulphur trioxide are always produced in the parallel cases. The arsenic oxide, which may amount to 1/30th of the whole, seems to be formed directly from arsenic, since arsenious oxide cannot be oxidised under the conditions. The author assumes conversely that arsenic oxide is the sole original product, and this is mainly decomposed into arsenious oxide by a secondary change.

The synthesis of sulphur chloride and arsenic chloride without incandescence is unaccompanied by ionisation. R. J. C.

Formation of Silicon Sulphide in the Desulphurisation of Iron. W. FIELDING (*Trans. Faraday Soc.*, 1909, **5**, 110—111).—The object was to find the conditions under which ferrosilicon can react with ferrous sulphide and liberate a sulphide of silicon. The reaction was investigated by heating mixtures of the two compounds in a vacuum at known temperatures. The heating was effected in a crucible in the form of a hollow graphite rod, heated electrically.

With commercial ferrous sulphide the mass fused at about 930°, and a vigorous reaction set in, accompanied by a rise in temperature. With pure ferrous sulphide, no reaction was observed up to about 1300°, so that the reaction noted with the impure compound was probably due to reduction of oxide of iron present by the ferrosilicon.

In all the experiments a yellow sublimate appeared on the walls of the tube at 1500°. This was found to consist of approximately 50% of silicon sulphide (assuming the formula to be SiS_2), the remainder being iron sulphide which had volatilised, silica resulting from the action of moisture in the air on the silicon sulphide, and a small amount of

finely-divided ferric oxide. In different experiments products of variable composition were obtained, and it has not been possible completely to identify the silicon sulphide present in the product.

T. S. P.

Thermal Analysis of the System K_2SO_4–KF. B. KARANDÉEFF (*Centr. Min.*, 1909, 728—733).—On the basis of observations on the rate of cooling of fused mixtures of potassium sulphate and potassium fluoride, a temperature concentration diagram has been constructed. The freezing-point curve consists of three branches corresponding with the two components and with a double salt, KF,K_2SO_4, respectively. The eutectic temperatures, 883° and 788°, correspond respectively with 41 and 83 mols.% of potassium fluoride. The double salt melts at 887°. It is only stable at temperatures above 578°, and on cooling below this, breaks up into its components. Potassium sulphate undergoes a change in crystalline form at 599°.

H. M. D.

Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation. E. H. RIESENFELD and B. REINHOLD (*Ber.*, 1909, **42**, 4377—4383).—According to the authors, Constam and von Hansen (Abstr., 1897, ii, 550) did not definitely prove that the substance which formed at the anode in the electrolysis of concentrated solutions of potassium carbonate was potassium percarbonate. The substance was never obtained pure, the hydrogen carbonate and water being always present, so that it was possible that it was a hydrogen peroxide additive product of potassium carbonate, since the authors have recently proved the anodic formation of hydrogen peroxide in strong solutions of potassium hydroxide at low temperatures (compare Abstr., 1909, ii, 879).

The authors have now succeeded in preparing a pure potassium percarbonate of the formula $K_2C_2O_6$, and containing neither water nor hydrogen carbonate, so that it could not be an additive product of hydrogen peroxide. It was made by the electrolysis at $-30°$ to $-40°$ of a very strong solution of potassium carbonate, contained in a U-tube. The anode was a platinum wire, the cathode being of platinum foil and surrounded by parchment paper. The current used was 0·5 ampere. After six hours the salt formed at the anode was collected, washed with cold water, alcohol, and ether, and dried, and then proved to have the composition given above. When added to a neutral solution of potassium iodide at the ordinary temperature, it immediately liberates iodine according to the equation :

$$C_2O_6'' + 2I' = 2CO_3'' + I_2,$$

no oxygen being evolved, whereas hydrogen peroxide reacts very slowly under such conditions. This reaction is characteristic of a real percarbonate, and can be used to distinguish them from additive products of carbonates and hydrogen peroxide. It is found that the percarbonates described by Tanatar (Abstr., 1903, ii, 208), when added to a neutral solution of potassium iodide, cause a brisk evolution of oxygen, and the solution remains colourless. All these compounds

must therefore be classed as additive products of hydrogen peroxide and carbonates. The percarbonates obtained by Wolffenstein and Peltner (Abstr., 1908, ii, 180, 183; 1909, ii, 574) are also doubtful.

It was not found possible to prepare solid percarbonates of lithium, sodium, rubidium, and cæsium, although the anolyte reacted towards potassium iodide as if it contained percarbonate. T. S. P.

Reduction of Sodium Sulphate by Carbon. ALBERT COLSON (*Compt. rend.*, 1909, **149**, 1076—1078).—When an intimate mixture of sodium sulphate and animal charcoal is heated in an iron pipe, practically no interaction takes place below 950°, but at this temperature the reduction is rapid and uniform, especially if charcoal is used in the proportion required by the equation: $Na_2SO_4 + 4C = Na_2S + 4CO$. With increase of temperature, the rate of action augments rapidly. T. A. H.

Action of Safety Explosives containing Ammonium Nitrate in the Presence of Carbon, Paper, and Paraffin. H. DAUTRICHE (*Compt. rend.*, 1909, **149**, 926—928).—Safety explosives containing ammonium nitrate are used in coal mines, and since oxygen is set free in the explosion, it is important to investigate their action on charcoal powder, which would be equivalent to coal dust in the mine, and on paper and paraffin, the latter being used in making the cartridges.

Experiments carried out under conditions very similar to those obtaining in a mine, with an explosive consisting of 90 parts of ammonium nitrate to 7 parts of trinitrotoluene, show that charcoal powder surrounding the cartridges is burnt, and that all the oxygen is used up with the formation of carbon monoxide. The combustion of the paper and paraffin depends on the diameter of the cartridges. When these are 30 mm. in diameter, the combustion is feeble, but when 40 mm. in diameter, it is very marked. T. S. P.

True Atomic Weights. Stas' Determinations. III. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], **5**, 1049—1053, 1053—1055, 1055—1058).—A series of three papers continuing (this vol., ii, 886) the critical revision of Stas' determinations, the cases now considered being (1) silver iodate, (2) silver bromate, (3) silver chlorate.

The apparent atomic weights found for the three cases are: (1) silver 107·9990 and 107·9991, iodine 126·9790 and 126·9991, oxygen 16·0149 and 16·0128, (2) silver 107·9995, bromine 79 9995, and oxygen 16·0061, (3) silver 107·9996, chlorine 35 4996, and oxygen 16·0036. T. A. H.

So-called Electrolytic Peroxide of Silver. MARGRETE BOSE (*Zeitsch. physikal. Chem.*, 1909, **68**, 383—384).—The author's work on the same subject (compare Abstr., 1905, ii, 299) has not been mentioned by Baborovsky and Kuzma (compare Abstr., 1909, ii, 666). G. S.

Silver and Thallium Iridichlorides and Iridochlorides. MARCEL DELÉPINE (*Compt. rend.*, 1909, **149**, 1072—1074. Compare Abstr., 1908, ii, 702).—The fugitive blue precipitate formed when potassium

iridichloride is added to silver nitrate consists of silver iridichloride, Ag_2IrCl_6. This when kept, either alone or in presence of excess of silver nitrate, passes into silver iridochloride, Ag_3IrCl_6, which is yellow, and on treatment with ammonia changes into the greenish-yellow *argentodiammonium iridochloride*, $(Ag2NH_3)_3IrCl_6$, which loses part of its ammonia on exposure to air and the whole of it on warming (compare Claus, *J. pr. Chem.*, 1847, i, **42**, 348).

Thallium iridichloride, Tl_2IrCl_6, forms small, opaque, greenish-blue cubes, and is more stable than the corresponding silver salt. Boiling hydrochloric acid decomposes it, forming the *iridochloride*, Tl_3IrCl_6, which crystallises out, on cooling the liquid, in bronze-tinted lamellæ. Nitric acid re-converts it into the iridichloride. T. A. H.

The Calcium Silicides and their Absorptive Power for Nitrogen. ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1909, **64**, 342—367).—By heating together calcium and silicon, two silicides are obtained, according to the component in excess. The products contain 53·5% and 36·68% Si respectively, corresponding approximately with the formulæ Ca_6Si_{10} and $Ca_{11}Si_{10}$ (compare Hackspill, Abstr., 1908, ii, 589; Tamaru, Abstr., 1909, ii, 400). Both silicides are crystalline, evolve hydrogen with acetic acid, and evolve spontaneously inflammable hydrogen with dilute hydrochloric acid. Silicones are obtained with concentrated hydrochloric acid. The first silicide yields an orange or yellow, crystalline silicone, the second yields a silicone containing less silicon.

Both silicides absorb nitrogen actively near 1000°, the first compound being the more energetic. The products have the respective compositions $CaSi_2N_3$ and $Ca_{11}Si_{10}N_{10}$. Structural formulæ are proposed for the silicides, silicones, and silico-nitrides. C. H. D.

Calcium Ferrites. SIEGFRIED HILPERT and ERNST KOHLMEYER (*Ber.*, 1909, **42**, 4581—4594).—Mixtures of pure ferric oxide and lime are heated in a platinum crucible, protected by an outer crucible of spinel mass, in an electric furnace, of which a hollowed-out carbon rod forms one pole, the other being an outer iron cone, the space between being filled with granulated carbon.

Mixtures containing only small percentages of iron oxide are not completely fusible under these conditions, being on y pasty. The last portion solidifies at 1410°, when they become completely solid. The lime forms well-developed crystals. When the lime falls below 75 mol.%, the primary crystallisation is that of the orthoferrite. The first complete fusion is obtained with 69 mol.% CaO, freezing beginning at 1550°.

Calcium orthoferrite, $3CaO,Fe_2O_3$, melts at 1410°, and disintegrates, like calcium orthosilicate, on fuither cooling. The next compound, $3CaO,2Fe_2O_3$, melts at 1450°. At 1220° a reaction occurs in the solid state, the compound formed having a formula near to $5CaO,3Fe_2O_3$ (compare the aluminate, $5CaO,3Al_2O_3$: Shepherd, Rankin, and Wright, Abstr., 1909, ii, 1015). There is a eutectic point at 1200° and 50 mol.% CaO, and a second maximum at 1400°, corresponding with

the compound $2CaO,3Fe_2O_3$. *Calcium metaferrite*, CaO,Fe_2O_3, appears to be formed below the eutectic point. The behaviour of mixtures rich in ferric oxide is complicated, partly owing to the escape of oxygen and the formation of crystals of magnetite. Ferric oxide melts at 1565°, and the magnetic oxide at 1527°.

The colour of the mixtures becomes darker with increasing iron. The specific volume curve shows a sharp change of direction at the formula CaO,Fe_2O_3, and another, less distinct, near 20 mol.% CaO. The magnetic properties diminish with the proportion of iron, and become insignificant at 67 mol.% CaO. The electrical conductivity is very small throughout, even that of fused ferric oxide being only 10^{-10} that of iron. Solid solutions are not formed, and the low conductivity is unexplained.

The calcium ferrites are much less readily attacked by reagents than the silicates, hence the advantage of their presence in cements exposed to sea-water. The mixtures containing 60—70 mol.% CaO are hydraulic. Calcium ferrites are less easily reducible than ferric oxide. C. H. D.

Compounds containing Iron Peroxide, FeO_2. LUDWIG MOESER and H. BORCK (*Ber.*, 1909, **42**, 4279—4283. Compare Abstr., 1903, ii, 546).—When a mixture of concentrated solutions of ferric and strontium nitrates (1 mol. : 1—2 mols.) is evaporated to dryness, and the finely-powdered residue heated at a temperature of not more than 600° in a stream of oxygen until oxides of nitrogen are no longer evolved, a compound is obtained which seems to have the formula SrO,FeO_2. Determination of the proportion of active oxygen to ferric oxide showed that it could not be a compound of strontium peroxide and ferric oxide.

A similar compound was indicated in the residue obtained by heating a mixture of barium hydroxide and ferric hydroxide at 400° in a current of oxygen.

These compounds are black substances, which are stable below 650°, but decompose gradually above that temperature. They are slowly acted on by water with evolution of oxygen. Hydrogen peroxide reacts violently with liberation of oxygen; acids act in a similar manner. Hydrochloric acid gives both chlorine and oxygen; oxalic acid, oxygen and carbon dioxide. Mixtures of air and alcohol or other inflammable vapours, when led over the heated compounds, are oxidised to water and carbon dioxide, and when once the combustion has started, it proceeds of its own accord.

It is possible that a compound of iron peroxide with lithium oxide has been obtained, but it was not found possible to prepare such compounds with other bases.

In an appendix, H. Borck describes a compound of strontium and ferric oxides which is obtained, in a hydrated condition, as a yellowish-brown precipitate by warming a suspension of freshly-precipitated ferric hydroxide in a concentrated solution of strontium hydroxide for some time on the water-bath. On heating, it loses water and becomes brown, and at temperatures above 300° it absorbs oxygen, forming the compound SrO,FeO_2. T. S. P.

Hexahydrated Glucinum Sulphate. MARIO LEVI-MALVANO (*Gazzetta*, 1909, **39**, ii, 438—440. Compare Abstr., 1906, ii, 165).—The author gives a new example of crystallisation of one salt under the catalytic influence of another dissolved salt.

When prepared in the ordinary way, hexahydrated glucinum sulphate forms a mass of crystals incapable of being measured; but when a solution containing equimolecular proportions of glucinum and potassium sulphates is concentrated on the water-bath and allowed to cool, it deposits large crystals of hexahydrated glucinum sulphate belonging to the cubic system [ZAMBONINI], and melting partly at 78—80° and completely at 95—96°. T. H. P.

Basic Magnesium Chlorides. WILLIAM O. ROBINSON and W. H. WAGGAMAN (*J. Physical Chem.*, 1909, **13**, 673—678).—Solutions containing from 2·36 to 34·22% of magnesium chloride were shaken with small amounts of magnesium oxide for six months at a temperature of 25°. At the end of this time, the residues had become homogeneous, and the solutions constant in composition. From an examination of the diagram on which the solubility data are plotted, the conclusion is drawn that the solid substance in equilibrium with solutions containing less than about 10% of magnesium chloride is an indefinite solid solution, whereas the solid residue in contact with more concentrated solutions is a basic salt of the composition $3MgO,MgCl_2,10H_2O$. Microscopic examination showed that this consists of very small, acicular crystals. H. M. D.

Zinc Amalgams. ERNST COHEN and KATSUJI INOUYE (*Chem. Weekblad*, 1909, **6**, 921—930. Compare Roozeboom and Byl, Abstr., 1901, ii, 507; Kerp and Böttger, Abstr., 1900, ii, 656; Pushin, Abstr., 1903, ii, 212; Hulett, Abstr., 1900, ii, 543).—The authors have investigated the solubility of zinc in mercury at temperatures between 0° and 100°, and found that it increases. Kerp and Böttger's method gives erroneous results, especially between 20° and 100°. Pushin's results are also incorrect. A. J. W.

Double Fluorides of Univalent Thallium. FRITZ EPHRAIM and LEONID HEYMANN (*Ber.*, 1909, **42**, 4456—4463).—*Thallous manganosomanganic fluoride*, $5TlF,2MnF_3,MnF_2$, obtained by precipitating manganous acetate with ammonia and hydrogen peroxide, dissolving the well-washed precipitate in hydrofluoric acid, and adding thallous fluoride, forms claret-coloured prisms, decomposed by water, but soluble in cold concentrated sulphuric acid or in dilute oxalic or tartaric acids to violet solutions, decolorised on heating. Attempts to prepare the manganic compound result in the formation of this salt.

The three *antimony* compounds, TlF,SbF_3; $TlF,2SbF_3$, and $TlF,3SbF_3$, are all crystalline.

Thallous fluoride and an excess of a solution of vanadium pentoxide in hydrofluoric acid yield minute, insoluble crystals of the salt,

$$3TlF,2VO_2F.$$

By previously reducing the vanadium solution with sulphur dioxide,

small, green crystals of the salt, $2TlF,VOF_2$, are obtained, whilst reduction of the pentoxide with hydrogen, followed by solution in hydrofluoric acid and addition of thallous fluoride, leads to the formation of green crystals of $TlF,VF_3,2H_2O$ or of $2TlF,VF_3,H_2O$, according to the proportions taken.

The *thallous tantalum* compound, $2TlF,TaF_5$, forms bright glistening crystals.

Three *tungsten* compounds, $2TlF,WO_2F_2$, $3TlF,2WO_2F_2$, and TlF,WO_2F_2, are obtained by adding different proportions of thallous fluoride to a solution of tungstic acid in hydrofluoric acid.

C. H. D.

Conditions which Determine the Composition of Electro deposited Alloys. Part I. Copper-Zinc Alloys. SAMUEL FIELD (*Trans. Faraday Soc.*, 1909, 5, 172—194).—To trace the effect of varying conditions on the composition of electro-deposited alloys, the composition of electro-deposited brass, obtained from a cyanide solution under different conditions of (*a*) composition of solution, (*b*) strength of solution, (*c*) temperature, (*d*) current density, and (*e*) presence of free cyanide, was determined. The conditions for quantitative deposition from cyanide solutions of the metals separately were first found, and the solutions were then mixed. It was found that, with a solution containing about equal quantities of the two salts in the absence of any notable amount of free cyanide: (*a*) Copper is the more readily deposited. (*b*) The percentage of zinc increases with the current density, and also as the amount of zinc compound is increased. (*c*) Even with a large excess of zinc in the electrolyte, deposits containing a fair proportion of copper are readily obtained. (*d*) Dilution raises the percentage of zinc, because of the higher *E.M.F.* necessary to maintain the same current density. (*e*) Rise in temperature increases the proportion of copper deposited. (*f*) With appreciable amounts of free cyanide the percentage of copper is always high, even with high current density. Free cyanide does not increase the conductivity of the solution to any great extent, but it prevents the formation of insoluble single cyanides at the anode.

Uniform deposition is not maintained in cold stationary solutions, and the insoluble cyanides formed at the anode may completely insulate the plates. With a warm and moving solution, uniform deposits may be obtained without the presence of much free cyanide, the anodes dissolving freely. These cyanide solutions are subject to continual changes of composition which soon prevent the exact repetition of similar conditions. These changes are due to: (1) differing proportions of copper and zinc dissolved at the anodes and precipitated at the cathodes, and (2) to the different amounts of cyanide absorbed or set free by the metals.

The zinc compound used in the above experiments corresponded with the composition $Zn(CN)_2,KCN$, whilst the copper compound had the composition $CuCN,KCN$. This latter compound was obtained by saturating a hot solution of Kahlbaum's potassium cuprocyanide, of the composition $3CuCN,KCN + 5KCN$, with freshly precipitated copper carbonate, and then allowing it to crystallise.

T. S. P.

The Corrosion of Iron. J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1909, Reprint 3—7. Compare Abstr., 1908, ii, 698; Proc., 1909, **25**, 90).—A criticism of recent experiments on the rusting of iron. The presence of an acid is necessary to the initiation of rusting.

C. H. D.

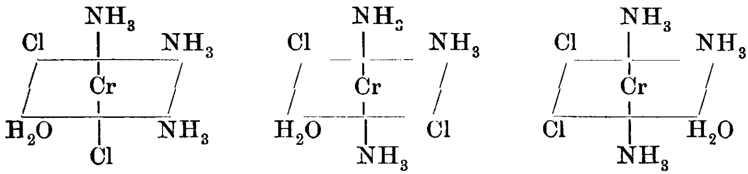
The Action of Air and Steam on Pure Iron. J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1909, Reprint 2—11. Compare preceding abstract).—At temperatures above 200°, pure iron oxidises in air dried by means of phosphoric oxide. Steam, carefully freed from carbon dioxide, is without action on iron at 100—250°. Slight action begins at 330°, and is rapid at 445°. Traces of air may have been present. Experiments in silica tubes indicate that the temperature at which action begins is near 350°. The action of steam probably takes place in two stages, the steam being first dissociated, and the oxygen thus set free acting on the iron. An estimate is made of the dissociation pressure of iron oxide. C. H. D.

Reduction of Iron Oxide by Hydrogen and Carbon Monoxide. SIEGFRIED HILPERT (*Ber.*, 1909, **42**, 4575—4581).—The temperature at which the reduction of ferric oxide by hydrogen begins, depends on the temperature to which the oxide has been previously heated. A sudden fall in the reducibility of oxide prepared from the hydroxide occurs at 900°, at which point there are indications of a polymorphic change. Oxide prepared from the oxalate only shows this change at 1000°. In both cases the final product behaves like natural hæmatite, and is only reduced from 330° onwards. It is impossible to obtain a product containing a determined quantity of oxygen by these means, as the reaction takes place unequally in different parts of the mass.

Carbon monoxide is active even at 240°, but the resulting oxide is impure, containing carbon. C. H. D.

Chromi-aquo-triammines. E. H. RIESENFELD and F. SEEMANN (*Ber.*, 1909, **42**, 4222—4232. Compare Abstr., 1906, ii, 760).—If chromtetroxide-triammine is added in small quantities at a time to a cooled dilute solution of hydrochloric acid, a violent reaction takes place, with evolution of oxygen and chlorine and formation of a red solution. Addition of concentrated hydrochloric acid to this solution produces, after a long time, a precipitate of dichloroaquotriammine-chromichloride, $\left[Cl_2Cr{}^{OH_2}_{(NH_3)_3}\right]Cl$, in the form of reddish-violet, dichroitic crystals, which are soluble in water to a blue solution. If concentrated hydrochloric acid is used instead of the dilute acid, a light green solution is obtained, from which grey, needle-shaped crystals of a second modification of the above chloride separate, which is scarcely soluble in cold water, but dissolves in hot water to a red solution. A third modification is obtained by heating a hydrochloric acid solution of the first chloride for some time at 60°. The solution gradually becomes green in colour, and on evaporation in a desiccator, dark green crystals are obtained, which dissolve in water to a green

solution. Neither of these three chlorides readily loses water, which is therefore probably contained in the complex in all three salts. In all probability they are stereoisomerides :



At present it is impossible to say which formula corresponds with which isomeride.

If the aqueous solution of either of the three isomeric chlorides is heated to the boiling point, the colour changes to a violet-red, and on careful evaporation, violet-red crystals of the chlorodiaquotriammine-chromichloride, $\left[(NH_3)_3Cr\begin{smallmatrix}(OH_2)_2\\ Cl\end{smallmatrix}\right]Cl_2$, are obtained. These crystals are readily soluble in water to a red solution, from which, by the addition of concentrated sulphuric acid and precipitation with alcohol, pale violet, hygroscopic crystals of the chlorodiaquotriamminechromi-sulphate, $\left[(NH_3)_3Cr\begin{smallmatrix}(OH_2)_2\\ Cl\end{smallmatrix}\right]SO_4$, are obtained.

Chromtetroxide-triammine dissolves in concentrated nitric acid to a red solution, from which rose-red crystals of nitro-diaquotriammine-chrominitrate, $\left[(NH_3)_3Cr\begin{smallmatrix}(OH_2)_2\\ NO_3\end{smallmatrix}\right](NO_3)_2$, separate.

Triaquotriamminechromichloride, $[(NH_3)_3Cr(H_2O)_3]Cl_3$, is obtained by dissolving chromtetroxytriammine in dilute hydrochloric acid and passing hydrogen chloride into the resulting solution. After a time, bright red, needle-shaped crystals of the triaquochloride separate. If the hydrogen chloride is passed in for too long a time, the solution becomes green in colour, and crystals, either of the dichroitic or of the grey monoaquochloride, are obtained. If the aqueous solution of the triaquochloride is treated with concentrated nitric acid, deep red crystals of the triaquotriammine-chromichloride nitrate,

$$\left[(NH_3)_3Cr(OH_2)_3\right]\begin{smallmatrix}Cl_2\\ NO_3\end{smallmatrix},$$

are obtained.

Each member of the series of the chromi-aquo-triammines, with the exception of the first, $[Cl_3Cr(NH_3)_3]$, has thus been obtained. The separate members are characterised by their different colours, not only as solids, but also in aqueous solution, and it is noteworthy that the colours are exactly analogous to those of the corresponding cobalt compounds, as shown by the following table :

	M = Co.	M = Cr.
$[(NH_3)_3M,H_2O]$	Bluish-green solution......	Bluish-green solution.
$[(NH_3)_3M,2H_2O]$	Reddish-blue ,, ...	Violet-red ,,
$[(NH_3)_3M,3H_2O]$	Purple ,, ...	Purple ,,

This similarity in colour is all the more remarkable since the ordinary cobalt and chromium salts are so different in colour. The conclusion is therefore drawn that the colour of a salt depends more

on its constitution than on the metal which forms part of the cation. Assuming that the atoms in the molecule are bound together by electrical forces, the constitution of the molecule will depend on its electron-content and on the distribution of the electrons. It follows that absorption (of light), electron-content, and the distribution of electrons are all closely connected, a conclusion which has been arrived at in quite another way from optical considerations.

T. S. P.

The Isomerism of the Stannic Acids. WERNER MECKLENBURGH (*Zeitsch. anorg. Chem.*, 1909, **64**, 368—374).—The two modifications of stannic acid are best regarded as colloidal substances, differing in the size of their particles, as suggested by van Bemmelen (Abstr., 1888, 1160; 1905, ii, 461). The greater adsorptive power and reactivity of the α-acid indicates that it has the finer structure. The absence of any direct relation of the β-acid to the crystalloid compounds of tin is evidence of its coarser structure. C. H. D.

Double Halogenides of Ter-, Quadri-, and Quinque-valent Antimony. FRITZ EPHRAIM and S. WEINBERG (*Ber.*, 1909, **42**, 4447—4456).—Derivatives of quadrivalent antimony have a great tendency to decompose into mixtures of compounds of ter- and quinque-valent antimony, with the exception of the thallium salt,

$$TlCl_3,TlCl,2SbCl_4,$$

which is stable (Ephraim and Barteczko, Abstr., 1909, ii, 236). The equilibrium $SbCl_3 + SbCl_5 \rightleftharpoons 2SbCl_4$ is greatly dependent on the temperature and on the possibility of ionisation, the addition of sulphuric acid or of salts favouring the tetrachloride.

On adding solid ammonium chloride to a fused mixture of antimony tri- and penta-chlorides, the liquid becomes black, and solidifies on cooling to a violet mass, which slowly loses its colour at the ordinary temperature, ultimately becoming white. The dark metastable salt is best obtained by pouring the hot mixture into chloroform; it then remains for some hours without change.

The *ammonium* compound of *antimony tetrabromide*, $(NH_4)_2SbBr_6$, prepared by adding the requisite quantity of bromine, followed by ammonium bromide, to a solution of antimony tribromide in concentrated hydrobromic acid, forms black octahedra, stable in air. The free *acid* was obtained in a state of doubtful purity.

A *ferric ammonium antimony chloride*, $9NH_4Cl,2FeCl_3,3SbCl_4$, is obtained by mixing the chlorides in concentrated hydrochloric acid, and forms black octahedra. It may be regarded as $3(NH_4)_2SbCl_6 + 3NH_4Cl,2FeCl_3$.

Compounds of antimony tri- and penta-halogenides with salts of alkylamines are also described. The *methylamine* compounds,

$$SbCl_3,NH_3MeCl$$

and $SbCl_5,NH_3MeCl$, form very large, colourless prisms and microscopic crystals respectively. The *bromide*, $2SbBr_3,3NH_3MeBr,3H_2O$, forms lemon-yellow, six-sided leaflets, and the *iodide*,

$$2SbI_3,3NH_3MeI,5H_2O,$$

forms yellowish-red leaflets with golden reflex.

The *ethylamine* compounds: $2SbBr_3,3NH_3EtBr$, a yellow salt containing water; $SbBr_3,NH_3EtBr$, dark red leaflets, and

$$2SbI_3,3NH_3EtI,$$

are described.

The following *diethylamine* compounds are described:

$$SbCl_3,NHEt_2,HCl,$$

long, transparent needles; $SbCl_5,NHEt_2,HCl$; $SbBr_3,NHEt_2,HBr$; $SbBr_5,2NHEt_2,HBr$, black crystals, violet in thin fragments; and $SbBr_5,NHEt_2,HBr$, garnet-red, rectangular crystals. C. H. D.

Effect of Ferric and Cupric Salt Solutions on Gold. W. J. McCaughey (*J. Amer. Chem. Soc.*, 1909, **31**, 1261—1270).—In the analysis of gold bullion containing a large proportion of tin, it was found that the gold could be most conveniently separated by precipitation with ferrous sulphate. The precipitate, however, still contained tin, and if sufficient hydrochloric acid was present to keep all the tin in solution, the gold was not completely precipitated.

Preliminary experiments having shown that gold is soluble in solutions of both ferric and stannic salts in presence of hydrochloric acid, an investigation was carried out to ascertain the effect of the concentration of the salt and acid and the presence of ferrous sulphate on the solubility. The solvent action of cupric chloride was also studied. The experiments were conducted at 38—43° and at 98—100°. The results are tabulated and plotted as curves.

It has been found that gold is soluble in solutions of iron alum and cupric chloride containing hydrochloric acid, the solubility increasing with the concentration of the acid or salt. An increase in the concentration of the acid has a greater effect on the solubility than an increase in the concentration of the salt, and particularly in the case of the copper salt. The rate of solubility in the presence of iron alum is eleven times greater at 98—100° than at 38—43°, and in the presence of cupric chloride is 32 times greater at the higher temperature. By doubling the concentration of the acid, the solvent action of cupric chloride solution is increased seven times at 38—43° and five times at 98—100°. Iron alum is capable of dissolving gold even in presence of a ferrous salt, but the solvent action decreases as the concentration of the ferrous salt increases. In the precipitation of gold by ferrous sulphate, it is therefore advisable to use considerable excess of the reagent, and to allow the solution to cool before filtering it, since the solvent action of ferric salts is much greater at the higher temperatures. The solubility of gold in solutions of ferric salts gradually decreases with time and approaches a limit, but in the case of cupric chloride the amount of gold dissolved is directly proportional to the time. E. G.

Gold Hydrosols. Carl Thomae (*J. pr. Chim.*, 1909, [ii], **80**, 518—520).—Zsigmondy's red-gold hydrosol, which can be kept for a year, is prepared with water distilled repeatedly through a silver condenser. However, a hydrosol, which is tenable for four months, can be obtained with ordinary distilled water as follows. The water, 120 c.c., is brought to the boil in a Jena flask, and 2·5 c.c. of gold

chloride solution (1 gram of crystallised salt : 167) and 3·2 c.c. of potassium carbonate (2·5 : 100) are added successively. Whilst the water is boiling vigorously and the flask is being violently shaken, 5·0 c.c. of formaldehyde solution (3 grams of commercial approximately 36% formalin : 100) are added drop by drop. If the first drop causes a separation of gold, the addition is stopped, and the boiling is continued until the gold has disappeared. Gold should not separate until many drops of the formaldehyde have been added; then the formation of a slight gold mirror is immaterial. The liquid is blue at first, and finally dark red. It is decanted into another flask. The formation of a filminess or turbidity indicates that the reducing agent has been added too quickly, or in too large quantities. C. S.

Magnesium Aurides. G. G. URAZOFF (*Zeitsch. anorg. Chem.*, 1909, **64**, 375—396. Compare Vogel, Abstr., 1909, ii, 896).—Alloys of gold and magnesium are best prepared by heating the components in the proportions required to form the compound AuMg in a graphite crucible enclosed in an iron cylinder with screw cap. Combination takes place readily at 700°, and the compound may be fused quietly with further quantities of gold or magnesium under a layer of alkali chloride.

Four compounds are indicated on the freezing-point curve: AuMg, with a maximum at 1150°; $AuMg_2$, with a maximum at 788°; Au_2Mg_5, at a break in the curve at 798°, and $AuMg_3$, with a third maximum at 818°. Gold forms solid solutions with nearly 30 atomic % Mg, and the compound AuMg forms solid solutions ranging from 42 to 66 atomic % Au. The compound Au_2Mg_5 undergoes a transformation at 721°.

Alloys rich in gold may be etched with hydrochloric acid and bromine; those containing little gold are etched sufficiently by polishing while wet. The microscopical examination confirms the indications of the cooling curves. C. H. D.

Atomic Weight of Platinum. EBENEZER H. ARCHIBALD (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721—747).—From a consideration of earlier determinations, the author draws the conclusion that the platinum salts analysed must have contained appreciable amounts of impurities, for very divergent results are obtained when the weight of original salt is used in the calculation of the atomic weight. To obtain pure platinum the metal was precipitated in the form of ammonium platinichloride, the precipitate being thoroughly washed and dried and then reduced in a current of pure hydrogen. After removal of ammonium chloride, the platinum-black was boiled with successive portions of concentrated hydrochloric acid to dissolve out traces of iron. The platinum was then redissolved, and the above processes repeated several times. After three operations all indications of iridium had disappeared. To avoid the difficulty of removing the last traces of nitric acid from a solution prepared by dissolving platinum in aqua regia, the metal was brought into solution by making it the anode in an electrolytic cell containing hydrochloric or hydrobromic acid. From such solutions the potassium and ammonium salts of chloro- and bromo-platinic acid

were prepared. With these four salts, four series of determinations were made by reduction in a current of pure dry hydrogen. Before reduction the potassium salts were heated at 400°, and the ammonium salts at 175°, for the purpose of expelling absorbed and occluded moisture. After reduction, the platinum metal, the halogen salt, and the halogen acid given off were estimated. These measurements give several ratios from which the atomic weight of platinum can be deduced. Rejecting those in which the weight of original salt is concerned, twelve values are obtained for the atomic weight, the lowest of which is 195·21, and the highest, 195·24. The mean value adopted is 195·23. ($O = 16$.)

Incidentally, it is shown that the same results are obtained for the weight of reduced platinum, whether this is heated and cooled in hydrogen and weighed at atmospheric pressure, or heated, cooled, and weighed in a vacuum. H. M. D.

Metallic Iridium Disulphates. MARCEL DELÉPINE (*Compt. rend.*, 1909, **149**, 785—788; *Bull. Soc. chim.*, 1909, [iv], **5**, 1084—1088, 1126—1133. Compare Abstr., 1909, ii, 408).—The action of sulphuric acid on potassium iridochloride gives a blue solution which does not contain a salt of the same type as the ammonium iridium disulphates already described. The ammonium in the latter can, however, be wholly or partly replaced by potassium, sodium, thallium, and barium.

The iridium disulphates fall into two series, namely, the green salts, which are generally acidic, derived from the acid,

$$H_2[Ir(SO_4)_2(OH)H_2O],$$

designated H_2A'', and the reddish-brown salts, which are basic, derived from the acid, $H_3[Ir(SO_4)_2(OH)_2]$, designated H_3A'''. These tautomeric acids are easily converted into one another by addition of excess of base and acid respectively.

The following basic salts are described: $K_7H_2(A''')_3,6H_2O$, crystallising in needles varying in colour from old rose to blackish-brown, according to thickness. This salt is prepared by pouring a cold solution of $NH_4 \cdot H_3(A'')_2$ into excess of potassium carbonate solution. $Na_7H_2(A''')_3,6H_2O$ and $9H_2O$, reddish-brown clusters of needles or rectangular plates, is obtained by precipitation with alcohol. $Tl_{21}(NH_4)_7H_8(A''')_{12}$ and $Tl_7H_2(A''')_3,4\frac{1}{2}H_2O$, dark brown crystals, are very slightly soluble. $Ba_7H_4(A''')_6,Aq$ is a greenish-brown, amorphous precipitate, turning pure green on exposure to air and slowly depositing barium sulphate.

The salts of the acid H_2A'' are all soluble in water, but less soluble in presence of alcohol, ether, or another salt of the same metal. The following were prepared by a variety of methods from the corresponding ammonium salts: $K_8NH_4H_3(A'')_6,3H_2O$, green to black needles according to size. $K_4H_2(A'')_3,1\frac{1}{2}H_2O$, needles.

$$K_5H(A''')_3,3H_2O,$$

hexagonal or octahedral crystals. $K_2(A''),H_2O$, opaque, square crystals, very dark green; their solution is alkaline, and of an impure green colour. $K_2H_4(A'')_3,6H_2O$, tetrahedra, stable only in strong acids. $Na_8 \cdot NH_4 \cdot H_3(A'')_6,18H_2O$, very soluble black crystals, almost

rectangular. $Tl_7(NH_4)_2H_3(A'')_6$ to $Tl_7H_5(A'')_6,6H_2O$, a mixture consisting of small, green needles, only slightly soluble in water.

$$Ba_2H_2(A'')_3,12H_2O,$$

crystallising in long, green needles or black, rectangular crystals.

$$Ba(NH_4)_2(A'')_2,2H_2O,$$

small, opaque, black tetrahedra. R. J. C.

Osmium. ALEXANDER GUTBIER and K. MAISCH (*Ber.*, 1909, **42**, 4239—4243).—In preparation for a revision of the atomic weight of osmium, the authors have submitted the osmichlorides to a systematic investigation. Sodium osmichloride was first prepared by heating a mixture of sodium chloride and osmium in a current of chlorine. If the osmium is in the form of granules, the reaction takes place extremely slowly, but when the metal is in a finely divided condition, the reaction is complete in about half-an-hour at a red heat. The sintered mass which is thus obtained was dissolved in cold dilute hydrochloric acid, the solution filtered, and the filtrate saturated with hydrogen chloride to precipitate any sodium chloride present. After further filtration, the sodium osmichloride was obtained by careful evaporation of the filtrate; this salt could not, however, be prepared in a quite pure condition. It was therefore used to prepare the osmichlorides of ammonium, potassium, rubidium, and cæsium by double decomposition with the chlorides of these metals. All these compounds are much less soluble than sodium osmichloride, and, after recrystallisation from dilute hydrochloric acid, they are obtained as dark-coloured, well-defined, octahedral crystals which are stable in dry air; on being powdered they each give a bright red powder. They are soluble in cold water, but the solutions decompose on exposure to the air, after a time depositing a black powder. They are easily soluble in dilute hydrochloric acid, giving stable solutions.

With the exception of the sodium salt, all these compounds are anhydrous. T. S. P.

Mineralogical Chemistry.

The Need for a Systematic Study of Optically Active Petroleums. MICHAEL RAKUSIN (*Ber.*, 1909, 42, 4675—4678. Compare Abstr., 1909, ii, 246, 490, 586).—Mainly polemical. A reply to Ubbelohde (Abstr., 1909, ii, 899). J. J. S.

Selenium in Altai Minerals. P. P. PILIPENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 1113—1115).—Two samples of galena from the Altai mountains were found to have the following compositions:

	Se.	S.	Pb.	Cu.	Fe.	SiO_2.	Total.
I.	1·17	12·60	82·28	1·28	0·48	2·02	99·83
II.	1·23	13·40	83·72	0·34	0·47	0·48	99·64

The mean composition, given by two analyses, of a sample of grey copper from a mine in the Altai district is as follows:

Se.	S.	Sb.	As.	Cu.	Ag.	Fe.	Co.	Zn.	SiO_2.	Total.
0·13	24·48	25·71	1·68	39·16	trace	2·00	0·23	4·87	0·95	99·21

A number of other Altai minerals, and also the sulphide compounds of the Mineralogical Museum of Tomsk University, were examined, but the above specimens were the only ones containing selenium.

T. H. P.

A Pitchblende probably occurring in New South Wales. T. H. LABY (*J. Roy. Soc. New South Wales*, 1909, **43**, 28—33).—The author has examined a pitchblende which was probably obtained from the New England district of New South Wales, although the exact locality is unknown. Analysis of the mineral gave:

UO_3.	UO_2.	PbO.	Mn_3O_4.	Fe_2O_3.	CaO.	Bi_2O_3.	CuO.	As_2O_3.	MgO.	SiO_2.	Insoluble.	H_2O (130°).
69·0	8·8	6·0	4·2	2·7	3·7	0·4	0·1	trace	trace	0·1	2·4	0·69

The powdered mineral has D^{23} 7·65. Its radioactivity is 4·4 times that which would result from the amount of uranium present. The absence of rare earths, the presence of CuO, Br_2O_3, and As_2O_3, the large proportion of UO_3, and the massive and non-crystalline form of the mineral indicate that it is probably a secondary pitchblende.

H. M. D.

Rhodizite in the Pegmatites of Madagascar. ALFRED LACROIX (*Compt. rend.*, 1909, **149**, 896—899).—The author has recently noted the presence of the two borates, danburite (Abstr., 1909, ii, 812) and hambergite ($BO_3Gl_2{\cdot}OH$), in the pegmatites of Madagascar. Tetrahedral crystals, $1\frac{1}{2}$ cm. across, of rhodizite have now been found embedded in the gem spodumene of a pegmatite-vein at Antandrokomby; the pegmatite is composed also of quartz, microcline, albite, red and yellow tourmaline, and a tantalocolumbate, probably identical with microlite. The rhodizite crystals are whitish-yellow with a tinge of green; they are pseudo-cubic, with optical anomalies similar to those of boracite. Mean refractive index (Na) 1·69, H 8, D 3·305. Analysis by F. Pisani gave:

B_2O_3.	Al_2O_3.	GlO.	Li_2O.	K_2O (+Cs_2O).	Na_2O.	SiO_2.	Loss on ignition.	Total.
40·60	30·50	10·10	7·30	5·90	3·30	1·36	0·45	99·51

Deducting silica and the corresponding amount of alumina and lithia, present as admixed spodumene, this analysis gives the formula $6B_2O_3,3Al_2O_3,4GlO,4(Li,K,Na,H)_2O$.

Damour's analysis (1882), made on only a small quantity of the rare and minute crystals of the Uralian rhodizite, showed no glucinum or lithium; it is remarked, however, that his percentage of alumina (41·40) is equal to the sum of the alumina and glucina in the above analysis, and a qualitative test now made on a Uralian crystal showed the presence of lithia.

L. J. S.

Pucherite from West Australia. E. GRIFFITHS (*J. Roy. Soc. New South Wales*, 1908, **42**, 251—252).—The concentrates from an oxidised quartz reef at Niagara, 115 miles north of Kalgoorlie, W. A., have been found to contain pucherite in the form of approximately cubical, crystalline grains, chrome-yellow in colour, brittle, and with a resinous lustre, D 5·7. Analysis gave the following results: Bi_2O_3 73·77%, V_2O_5 (including trace of P_2O_5) 25·31%, Fe_2O_3 0·36%, residue insoluble in hydrochloric acid 0·81%. H. M. D.

Connellite and Chalcophyllite from Bisbee, Arizona. CHARLES PALACHE and H. E. MERWIN (*Amer. J. Sci.*, 1909, [iv], **28**, 537—540).—A single small specimen from the Calumet and Arizona mine at Bisbee consists of groups of radiating needles of dark blue connellite together with cuprite, melanochalcite, and chalcophyllite. The connellite prisms are terminated by the unit pyramid, and measurements gave $a : c = 1 : 1·185$; refractive indices ω 1·724, ϵ 1·746; D 3·396. Analysis (by Merwin) on 0·73 gram gave:

SO_3.	Cl.	CuO.	H_2O (<220°).	H_2O (220—260°).	H_2O (260—300°).	H_2O (>300°).	Total (less O for Cl).
3·43	6·37	75·96	0·25	12·06	2·10	1·66	100·41

This differs somewhat from the only analysis previously made of connellite (Penfield, 1890, on only 0·074 gram), and corresponds with $Cu_{22}Cl_4SO_{23}.20H_2O$, or, distributing the water in accordance with the temperatures at which it is expelled,

$$[CuSO_4,3Cu(OH)_2,H_2O],2[CuCl_2,Cu(OH)_2],14[Cu(OH)_2].$$

The crystals of chalcophyllite present many points of resemblance to spangolite, but they were found to contain copper, aluminium, and arsenic. Measurements gave $a : c = 1 : 2·671$. L. J. S.

The Earths of Euxenite. OTTO HAUSER and FRITZ WIRTH (*Ber.*, 1909, **42**, 4443—4447).—Specimens of euxenite from (I) Eitland, (II) Arendal, (III) Saetersdal, (IV) South Carolina, gave the following analyses:

	Cb_2O_5.	Ta_2O_5.	TiO_2.	SnO_2.	WO_3.	UO_2.	ThO_2.	Y_2O_3.
I.	29·00	1·01	24·43	0·11	trace	5·64	4·60	27·32
II.	30·21		26·45	—	—	5·28	3·20	28·47
III.	20·72		31·45	0·13	0·09	5·49	3·80	25·42
IV.	28·20	9·35	17·45	0·07	0·11	7·91	2·04	22·01

	Ce(Sa,Di)$_2O_3$.	Al_2O_3.	FeO.	CaO.	MgO.	PbO.	Loss on ignition.	Total.
I.	2·45	trace	1·37	0·85	0·08	0·43	2·87	100·16
II.	2·05	—	1·89	0·97	—	—	2·01	100·64
III.	2·58	—	4·94	0·66	0·14	0·46	3·88	99·76
IV.	6·93	—	2·04	—	—	0·96	2·21	99·28

Of these, I and II are typical euxenites, III is to be regarded rather as a polycrase, whilst IV differs from both in containing an unusually large quantity of tantalic acid and a relatively small quantity of titanic acid.

Of the yttrium group, yttrium is always in excess. With increasing

titanium, holmium and dysprosium increase relatively to neo-erbium. The components of ytterbium are abundant, and scandium occurs, especially in polycrase, where it attains 0·06%. Samarium and praseodymium are absent from normal euxenites, but samarium is found with increasing tantalic acid. Zirconium could not be detected in any of the specimens. C. H. D.

Bertrandite from Altai. P. P. Pilipenko (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 1116—1118).—The author describes crystals of bertrandite occurring in the aquamarine deposits of the Altai mountains. The crystals have a glassy lustre, are mostly colourless and transparent, and form either long plates or prisms elongated along the *z* axis; $D^{15\,6}$ 2·603, hardness 6. Their composition is as follows:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	GlO.	H_2O.	Total.
50·12	trace	trace	trace	40·67	8·87	99·86

This bertrandite is formed as a result of the weathering of beryl, and itself undergoes further change. T. H. P.

Sardinian Minerals: Species from the Province of Sassari. Aurelio Serra (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 348—350. Compare Abstr., 1909, ii, 492, 494).—A sample of heulandite, in which the angle 110 : 1$\bar{1}$0 had a value of about 47°, was found to have the composition:

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
61·12	15·61	6·04	0·53	2·23	0·94	14·32	100·79

corresponding with the formula $(Ca,Mg,Na,K)O,Al_2O_3,SiO_2,5H_2O$. As typical heulandite contains SiO_2, 59 2; Al_2O_3, 16·8; CaO, 9·2, and H_2O, 14·8%, the abnormal value of the angle 110 : 1$\bar{1}$0 depends on the variations in chemical composition.

A sample of mesolite from "Su Marralzu" gave on analysis:

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
50·85	21·95	12·02	0·08	1·72	trace	14·61	101·23

and a sample of Smithsonite from the Sos Enattos (Lula) mines:

ZnO.	FeO.	CaO.	CO_2.	Total.
62·60	1 22	1·53	35·77	101·12

T. H. P.

Lujaurites from Pilandsberg (Transvaal). H. A. Brouwer (*Compt. rend.*, 1909, **149**, 1006—1008).—The analyses of two different kinds of lujaurite from the Transvaal are given. The one (I) is very similar to lujaurite from the Kola peninsula (Lapland), whilst the other (II) is rich in ægyrine and eudialyte:

	SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I.	52·35	0·59	0·39	14·11	7·98	2·17	0·62	4·65
II.	51·35	2·75	0·54	11·45	9·40	2·41	1·25	3 27

	MgO.	K_2O.	Na_2O.	CO_2.	H_2O.	Total.
I.	0·66	2·78	9 30	1·50	3·20	100·30
II.	0·54	2·52	10·80	—	3·20	99·48

As compared with other lujaurites, these are rich in lime, because of the presence of calcite. The decrease in Al_2O_3 and increase of Fe_2O_3 in (II) as compared with (I) is due to the former being rich in ægyrine. T. S. P.

Rhönite from Puy de Barneire at Saint-Sandoux. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1909, **32**, 325—331. Compare Abstr., 1907, ii, 972; 1909, ii, 587).—Large, black crystals with a brilliant greasy to metallic lustre are present in a doleritic nephelinite at this locality. Under the microscope these resemble the rhönite of the Rhön mountains, but owing to the depth of colour and intense pleochroism, their optical characters could not be completely determined; D 3·56. The following analysis by F. Pisani gives the formula: $(Na,K,H)_2Ca_8(Fe,Mg)_{15}(Al,Fe)_{16}(Si,Ti)_{21}O_{90}$.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
30·90	8·04	17·65	6·80	15·20	9·08	12·20	0·76	0·61	0·20	100·64

L. J. S.

Deposits from the Mineral Water of the Rohitsch Springs, Styria. HANS LEITMEIER (*Zeitsch. Kryst. Min.*, 1909, **47**, 104—123). —The waters of the springs at Rohitsch contain carbon dioxide with considerable amounts of magnesium carbonate, sodium sulphate and carbonate, and much less calcium carbonate, etc. Fine crystal groups of aragonite have been deposited naturally by these waters, and quartz crystals, $\frac{1}{2}$ cm. in length, are also noted. The mineral water was allowed to evaporate slowly in the air at temperatures of 2°, 13°, and 20°. At the two higher temperatures, acicular, rhombic, crystals of $MgCO_3,3H_2O$ (anal. I), identical with the mineral nesquehonite, were formed after some days; and later there was a deposit of indistinct crystals of aragonite. When, however, the evaporation took place at the lower temperature (2°) there was, after one-and-a-half months, a deposit of large, tabular, monoclinic crystals of the pentahydrate, $MgCO_3,5H_2O$ (anal. II). This salt is not formed at temperatures above 6°. It commences to lose water in the air at 20°, and at 60°, four-fifths is lost; at 100° the loss is 44·68%, and at 300°, 51·69%. These crystals have the same geometrical constants

$$[a:b:c=1\cdot6079:1:0\cdot9524;\ \beta=78°36']$$

as the mineral lansfordite $(3MgCO_3,Mg(OH)_2,21H_2O)$, and as the supposed tetrahydrate of magnesium carbonate described by Marignac. These three thus appear to be identical, the analyses of the last two having been made on partly dehydrated material:

	MgO.	CaO.	CO_2.	H_2O.	Total.	Sp. gr
I.	28·52	—	[31·09]	40·03	99·64	1·854
II.	23·18	trace	25·21	51·69	100·08	1·688

L. J. S.

Physiological Chemistry.

Asphyxia in the Spinal Animal. R. KAYA and ERNEST H. STARLING (*J. Physiol.*, 1909, **39**, 346—353).—In asphyxia the increased tension of carbon dioxide in the blood excites the brain centres, including those in the bulb; this produces exaggerated attempts to breathe, and a rise of arterial pressure, but no injurious action on the heart. The convulsions which follow are due to excitation of the spinal centres by lack of oxygen, and the heart failure, which leads to a fall of pressure, is also due to the same cause.

W. D. H.

Supposed Presence of Carbon Monoxide in Normal Blood and in the Blood of Animals Anæsthetised with Chloroform. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, *B*, **81**, 515—528).—For detecting carbon monoxide, the authors use the spectroscopic test and the admittedly delicate method of Haldane. Carbon monoxide is not a normal constituent of blood-gases. Chloroform is not decomposed in the blood with the formation of carbon monoxide. Chloroform vapour contained in the blood-gases of anæsthetised animals yields carbon monoxide when these gases are passed over potash. The small quantities of iodine found in Desgrez and Niclaux's experiments, in which the normal blood-gases are passed over iodine pentoxide at 150°, are probably due to the decomposition of this substance at this temperature. G. S. W.

Comparison of the Hæmoglobin of certain Molluscs with that of Vertebrates. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1909, **22**, 495—505).—The hæmoglobin from various molluscs was compared with that obtained from *Scyllium* and the dog. It did not differ essentially from these, although certain minor differences were observed; the mollusc blood, for example, is more readily changed by 10% acetic acid, and less readily by 10% sodium hydroxide solution; it is also more difficult to obtain in crystalline form. S. B. S.

Effect of Temperature on the Dissociation Curve of Blood. JOSEPH BARCROFT and W. O. R. KING (*J. Physiol.*, 1909, **39**, 374—384). —Dissociation curves of undialysed hæmoglobin solution in water are given at different temperatures in the presence and absence of carbon dioxide; in a solution of potassium chloride, the presence of carbon dioxide is relatively more powerful in the reduction of hæmoglobin than in the removal of oxygen. In low forms of animal life, in which hæmoglobin is retained in store in muscles or nervous tissue, the oxygen can be withdrawn in case of need, for instance, in partial asphyxia or great activity; a favourable condition for the ready withdrawal of oxygen would be rise of temperature or rise of carbon dioxide tension. The influence of temperature is evident also in the blood. In muscular exercise, with its accompanying rise of tempera-

ture, in fever, and in inflammation, the organism, or part of it, requires oxygen at a more rapid rate than usual; the rise of body-temperature enables the blood to meet this demand, and is, in fact, the counterpart of vascular dilatation. W. D. H.

Hæmolysis. OSCAR GROS (*Arch. exp. Path. Pharm.*, 1909, **62**, 1—38).—Hæmolysis is due to two factors: (1) the death of the corpuscles; (2) to physico-chemical changes which lead to the passage of hæmoglobin out of them. The second factor can be best studied if the changes occur rapidly, as when caused by ammonia. The velocity of the change is then proportional to the concentration of the ammonia, and inversely proportional to the concentration of the blood. Various salts were studied in the same way at different temperatures. Various ions favour hæmolysis at 47·5° in the following order: $Na<Mg<K<Ca$; $Cl<SO_4$; and at 50°, $Mg<Na<K<Ca$; $Cl<SO_4$. The inhibitory action of serum on hæmolysis is not destroyed by heating to 65°. W. D. H.

The Disintegration and Life of Blood-platelets. H. DEETJEN (*Zeitsch. physiol. Chem.*, 1909, **63**, 1—26).—Blood-platelets from human blood can be isolated by collecting the blood between the object glass and cover slip, and washing with physiological saline. In this way the other elements can be removed; the platelets alone remain sticking to the glass. They rapidly disintegrate under ordinary conditions, but remain, however, intact if quartz is used instead of glass, and the saline solution is perfectly neutral. In the presence of minute traces of alkali ($C_{OH}=10^{-5}$) and of somewhat larger quantities of acid ($C_H=2\cdot10^{-4}$) they disintegrate. The action of the hydroxyl ions is indirect; they either influence a ferment or cause the liberation of a ferment which causes the disintegration of the platelets. This statement is made in consequence of the fact that even in the presence of alkali the platelets can under certain conditions remain intact. Thus, they are protected from disintegration by the presence of hirudin, manganese salts, Witte's peptone, and peroxides. From the investigations with hirudin, the conclusion is drawn that the platelets themselves secrete an enzyme, which leads finally to their destruction. The platelets after treatment with hirudin are not disintegrated by alkali, although they are by plasma. The destroying ferment is not identical with the blood-clotting ferment, although it is possibly with the pro-ferment. Manganese salts do not entirely inhibit the disintegration, but only retard it; on the other hand, they inhibit blood-clottings, owing perhaps to action on the pro-ferment. Witte's peptone paralyses the platelets, and thus inhibits the secretion of the ferment. Peroxides entirely inhibit the disintegration of the isolated ferments. The explanation of this fact is not obvious. By means of the peroxide method, the action of the living platelets can be demonstrated. The presence of a nucleus, nuclear membrane, and amœboid movement can then be shown. The disintegration of the platelets after removal from the blood-vessels is due to the evolution of carbon dioxide and the increased concentration of the

hydroxyl ions. The platelets from other animals are not all identical with those from man; those from the ape are very similar.

S B S.

Spectro-photometry of Blood. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1909, 63, 313—314).—Remarks on the usefulness of Hüfner's spectro-photometer. In spite of its faults, it gives good results in accustomed hands.

W. D. H.

Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids. GIUSEPPE BUGLIA and L. KARCZAG (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 374—380).—The authors have determined the influence of *d*-, *l*-, *i*-, and *r*-tartaric acids in various concentrations on the time of coagulation by heating of normal blood-serum and of blood-serum dialysed until it has become neutral.

All these acids have a marked influence on the coagulation, at first accelerating it, and subsequently retarding, and even absolutely preventing, it. *i*-Tartaric acid, which is dissociated to a less extent than the other acids, also produces less acceleration of the coagulation, and renders the serum non-coagulable in lower concentrations than with the active and racemic acids. With these three acids, which are approximately equally dissociated, the influences on the coagulation are about the same.

T. H. P.

The Laws of Digestion and Absorption. SVANTE ARRHENIUS (*Zeitsch. physiol. Chem.*, 1909, 63, 323—377).—A mathematical discussion of the laws relating to the velocity, etc., of digestive processes. The rule of the square root appears to play a dominating part. London's work on the subject is on the whole corroborated.

W. D. H.

The Enzymes concerned in Nuclein Metabolism in Human Organs. ALFRED SCHITTENHELM. **The Fate of Nucleic Acid contained in the Food of Normal Men.** FRANZ FRANK and ALFRED SCHITTENHELM. **The Occurrence and Importance of Allantoin in Human Urine.** ALFRED SCHITTENHELM and KARL WIENER. **The Enzymes Concerned in Nuclein Metabolism in Lupin Seedlings.** ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 63, 248—268, 269—282, 283—288, 289).—The capacity of the human liver and other organs to form uric acid is undoubted, and can be readily demonstrated in extracts by their action on guanine. Commenting on W. Jones' statement regarding the absence of adenase in human organs, it is pointed out that unquestionably adenine disappears during life, the urine containing only traces after abundant ingestion of that substance when sweetbread is taken as food. It is therefore doubtful whether the action of extracts is a true index of vital metabolism; if an extract gives a positive result, it is no doubt of the same nature as that occurring during life; but if a negative result occur, that does not necessarily mean that a positive result may not occur during actual metabolism in the living organ. It is quite true, again, that extracts of human organs contain no uricolytic

enzyme, that is to say, destruction of uric acid does not occur post-mortem ; it is unscientific to conclude from this, that uricolysis does not occur during life.

Both in animals and men, nucleic acid given in the food is completely absorbed and undergoes metabolism, and the end-products are excreted during the same day. This comes out quite clearly by a study of nitrogen and phosphorus excretion. The proportion between the different end-products varies in different animals; in man, the main one is urea, the uric acid formed is small in amount, and the purine bases of the urine are minimal. The uric acid formed is doubtless again largely destroyed, and the nitrogen finally is contained in urea.

The meaning of allantoin in the urine is far from clear; if uric acid precursors are administered, the amount of allantoin does not increase in the urine. If allantoin is given by the mouth or subcutaneously, about 30% is recoverable in the urine. It cannot therefore be an important end-product of uric acid catabolism.

The expressed juice, or aqueous extracts of lupin seedlings, contain an amidase which converts guanine into xanthine. W. D. H.

The Elimination of Total Nitrogen, Urea, and Ammonia following the Administration of Amino-acids, Glycylglycine, and Glycylglycine Anhydride. PHŒBUS A. LEVENE and G. M. MEYER (*Amer. J. Physiol.*, 1909, **25**, 214—230).—The results of these metabolism experiments on dogs are given with full detail; the extra nitrogen administered is usually excreted within twenty-four hours, but this rate varies, and the proportion of urea, ammonia, etc., also varies in different cases. It is specially rapid after the ingestion of amino-acids. W. D. H.

The Influence of Removal of Segments of the Gastro-intestinal Tract on the Character of Protein Metabolism. ISAAC LEVIN, D. D. MANSON, and PHŒBUS A. LEVENE (*Amer. J. Physiol*, 1909, **25**, 231—253).—After excision of portions of the alimentary canal, an unexpected acceleration in the absorption and elimination of nitrogen is the most noteworthy result. W. D. H.

The Influence of Certain Mercury Compounds on Metabolism. GUIDO IZAR (*Biochem. Zeitsch.*, 1909, **22**, 371—393).—Mercury when introduced directly into the circulation, either in form of a hydrosol or of salts, markedly stimulates the nitrogenous metabolism, and the amount of nitrogen in the urine is considerably increased. Larger doses, however, of sublimate, calomel, hygrol, and mercuric thiosulphate are necessary to produce the same effect as a given dose of the hydrosol. There is no difference between the actions of stabilised and non-stabilised colloids. The increase of urea and uric acid in the urine runs parallel with the increase in total nitrogen. S. B. S.

[The Permeability of Cells for Dyes.] W. RUHLAND (*Biochem. Zeitsch.*, 1909, **22**, 409—410).—The author objects to the attempted explanation of Höber (Abstr., 1909, ii, 912) of the reason why wool-

violet-S and other dyes do not behave in accordance with the Overton lipoid theory. S. B. S.

Nucleo-protein in the Yolk Platelets of the Frog's Egg; and the Black Pigment. J. E. McClendon (*Amer. J. Physiol.*, 1909, **25**, 195—198).—The nucleo-protein investigated is probably more properly to be considered a lecitho-protein or vitellin-like substance. It is termed *batrachiolin*; it contains P 1·2%, S 1·32%, and N 15·14%. Analyses are also given of the black pigment which appears to belong to the melanins, but it was not satisfactorily freed from impurities. W. D. H.

The Catalase of Echinoderm Eggs before and after Fertilisation. Elias P. Lyon (*Amer. J. Physiol.*, 1909, **25**, 199—203).—If the eggs are treated with hydrogen peroxide, much more oxygen is set free by eggs which have been fertilised than by unfertilised eggs. The maximum is reached in twenty minutes after fertilisation. The increase in catalase is due either to a kinase in the sperm cell, or by an increase in the permeability of the egg, so that peroxide and catalase come more easily together. W. D. H.

[Analyses of Brains. Distribution of Sulphur in Brains.] Waldemar Koch (*J. Amer. Chem. Soc.*, 1909, **31**, 1329—1335). Waldemar Koch and Fred. W. Upson (*ibid.*, 1355—1364)—See this vol., ii, 78, 79.

The Action of Certain Salts on Frogs' Motor Nerves. G. Liljestrand (*Skand. Archiv. Physiol.*, 1909, **22**, 339—348).—Magnesium sulphate and chloride paralyse the motor nerves of the frog, but this occurs late and is preceded by a stimulating action. Weak solutions are not stimulating. Sodium chloride has a similar action. Zinc chloride acts in the same way, but much more strongly. W. D. H.

Influence of Different Substances on the Gaseous Exchange of the Surviving Muscular Tissue of Frogs. I. and II. Torsten Thunberg (*Skand. Archiv. Physiol.*, 1909, **22**, 406—429, 430—436).—I. The measurements were made by means of the author's micro-respirometer, generally in an atmosphere of oxygen. In the intact muscular tissue, the gaseous exchange is less than that of muscular tissue which has been cut by scissors; it is greater, however, than in muscular tissue which has been ground up with sand, so as to destroy the cell structure. Previous extraction of the tissue with physiological saline caused a marked diminution of the gaseous exchange; with isotonic neutral potassium phosphate, the diminution was less. The maximum of gaseous exchange takes place in isotonic saline; increase in the salt concentration causes a rapid diminution. There is not much difference in the gaseous exchange when the measurement is made after treatment with solutions of chlorides of the different alkali metals; the chlorides of the alkaline earths, on the other hand, cause considerable diminution. The action of the potassium halide salts is similar, with the exception of the fluoride, which causes a marked diminution in the gaseous exchange.

II. Oxalic, malonic, and succinic acids in the form of their potassium salts affect the gaseous exchange, considerably diminishing more especially the carbon dioxide output. The respiratory quotient is consequently affected by these salts. Other acids investigated do not affect the respiratory quotient in this manner. S. B. S.

The Formation of Carbon Dioxide in Surviving Tissues. OLAV HANSSEN (*Biochem. Zeitsch.*, 1909, **22**, 433—441).—The author gives a method for estimating the carbon dioxide evolved by surviving tissues (chiefly liver) when suspended in physiological saline at 37°. The influence of antiseptics and other substances on the action was determined. Certain substances, such as sodium β-hydroxybutyrate, caused increased carbon dioxide output. Sodium lactate caused a slight increase. Most other sodium and ammonium salts had but little action ; sodium glycollate, however, inhibited the output.
S. B. S.

Water Rigor in Frog's Muscle. EDWARD B. MEIGS (*J. Physiol.*, 1909, **39**, 385—390).—The statement of du Bois Reymond, that in water rigor of frog's muscle, as in other forms of rigor, sarcolactic acid is formed, was confirmed by the thiophen test. If the muscle is then placed in Ringer's solution, it loses acid and lengthens. This is regarded as a confirmation of the view that the acid is the cause, not the result or accompaniment, of the shortening. W. D. H.

Action of Cinchona Alkaloids on Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1909, xix—xxi ; *J. Physiol.*, **39**).—The relative toxicity of poisons can be well studied by their effect on the direct excitability of the frog's sartorius. In the case of the alkaloids examined, the figures obtained are : cinchonamine 400, quinine 100, quinidine 50, cinchonine and cinchonidine 25. These figures agree very well with what would have been anticipated from physicochemical data. W. D. H.

Extractives of Fish Muscle. FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1909, **63**, 104—105).—A reply to Suzuki and Yoshimura (Abstr., 1909, ii, 910).—The base, $C_5H_{11}O_2N$, isolated from *Ommastrephes* sp., agrees in properties with betaine and not with δ-aminovaleric acid, as stated by these authors. Furthermore, other bases described by them, such as arginine, leucine, lysine, and proline, have already been isolated in the author's laboratory from extracts of sea and land animals. S. B. S.

The Occurrence of Inactive Lactic Acid in a Meat Extract. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, **63**, 237—247).—Valentine's meat juice has a minimal nutritive value. Its colour is due to a pigment which was not identified, but is possibly a derivative of hæmoglobin. When kept, it deposits a crystalline precipitate of magnesium salts, among which lactate is present. The lactic acid is of the optically inactive kind. The freshly prepared juice contains sarcolactic acid, but as time goes on this is converted

almost completely into the inactive variety. Attempts to determine the cause of the transformation did not yield any certain results.

W. D. H.

The Nucleo-protein of Spleen. T. SATO (*Biochem. Zeitsch.*, 1909, 22, 489—494).—The nucleo-protein was prepared by precipitating the hot-water extract of the organ with dilute acetic acid. The amount of iron in various preparations varied between 0·15 and 0·80%. The metal appears to be contained in the nucleoprotein in two forms, namely, in a labile form, the part corresponding with which is removable from the substance by treatment with sodium carbonate, and a more stable form.

S. B. S.

Chemico-physical Investigations on the Crystalline Lens. XI. Imbibition of the Lens in Water at Different Temperatures and in Acids and Alkalis. FILIPPO BOTTAZZI and NOÉ SCALINCI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 327—339. Compare Abstr., 1909, ii, 502).—The velocity and total amount of imbibition of the crystalline lens in water are greater at high than at low temperatures. Imbibition in dilute solutions of an acid or an alkali increases with the concentration of the solution. In solutions of various acids and of sodium hydroxide, imbibition increases in the following order: acetic acid, sulphuric acid, water, hydrochloric acid, and sodium hydroxide. Since, in the concentrations employed, these acids are completely dissociated, the sulphuric and acetic anions must exert a specific depressing influence on the imbibition, in opposition to the action of the hydrogen ions which increase the imbibition. A similar relation probably holds with solutions of different bases, the accelerating influence of the hydroxyl ions on the imbibition being modified to varying extents according to the nature and valency of the cation.

When immersed in the acid solutions employed, the lens becomes opaque, probably owing to the precipitation of the faco-protein, which in its natural state is an electro-negative colloid, by the hydrogen ions. This action is more marked with sulphuric and acetic acids than with hydrochloric acid, which seems to be capable of transforming the alkaline faco-protein rapidly into acid.

T. H. P.

Chemico-physical Investigations on the Crystalline Lens. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 380—383). —The author has studied the influence of hydrochloric acid on the coagulation of the crystalline lens by the method previously employed with sodium hydroxide (Abstr., 1909, ii, 1036).

The curve of the velocity of coagulation in presence of hydrochloric acid is essentially similar to that obtained with sodium hydroxide, the variation in the velocity gradually diminishing as the amount of acid is increased; in this case, however, the final value of the velocity differs far less from the initial value than is the case when sodium hydroxide is present. Whilst the latter, up to a certain concentration, first increases and then sensibly diminishes the velocity of coagulation, hydrochloric acid produces a continuous increase.

The results indicate that the influence of chemical agents on the

velocity of coagulation of the crystalline lens is a function of the superficial area of the lens. T. H. P.

Chemical Investigation of Teeth. II. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1909, **63**, 397—400. Compare Abstr., 1908, ii, 609). —Teeth from prehistoric men (at least 2000 years old) were found to be well preserved. They contain 3% more organic substance than recent teeth, and less magnesium and phosphoric acid. The percentage of calcium, sodium, potassium, chlorine, and carbon dioxide is the same as in recent teeth. W. D. H.

Inorganic Constituents of Two Egyptian Mummies. PAUL HAAS (*Chem. News*, 1909, **100**, 296).—The constituents of the ash were as follows:

	CaO.	K_2O.	Na_2O.	Fe_2O_3.	Al_2O_3.	CO_2.	SO_3.	P_2O_5.	Cl.	SiO_2.	
Mummy A	4·83	1·21	0·24	0·156	0·134	2·64	1·91	1·57	0 22	—	per cent.
Mummy B	0·90	0·77	9·03	0·27	0·90	traces	2·99	0·42	1·89	5·80	,,

A hot-water extract of "A" had an acid reaction, and the same material yielded to ether 9% of extract, which was acid and soluble in potassium hydroxide solution. No arsenic, antimony, or mercury was present. The high percentage of lime in the ash from "A" may indicate that quicklime was added to the coffin in which the body was placed.

Material "B," unlike "A," was moist, and lost 16% of its weight when dried at 100°, but the dry material rapidly increased in weight on exposure to air. The ether extract amounted to 3·5%. In this case the embalming material may have been "natron," or "nitrum," a mixture of sodium chloride, sulphate, and carbonate. Alumina has not been recorded previously as a constituent of mummy ash.

T. A H

Presence of an Anæroxydase and Catalase in Milk. J. SARTHOU (*Compt. rend.*, 1909, **149**, 809—810.* Compare Bordas, Abstr., 1909, ii, 505).—The filtrate from milk curdled at 30° gives a very distinct reaction with *p*-phenylenediamine, but not with guaiacol or hydrogen peroxide. By treating the residue on the filter with water, a liquid is obtained which gives distinct colorations with *p*-phenylenediamine and guaiacol in presence of oxygen. The casein, after having been freed from the anæroxydase by washing, reacts with *p*-phenylenediamine and hydrogen peroxide, but not with guaiacol.

The conclusions drawn are that milk contains a soluble anæroxydase as well as an insoluble catalase, and that the excessive sensitiveness of *p*-phenylenediamine to oxidation should be recognised in the study of oxidising ferments. W. O. W.

Anæroxydase and Catalase in Milk. FRÉD. BORDAS and TOUPLAIN (*Compt. rend.*, 1909, **149**, 1011—1012. Compare Abstr., 1909, ii, 505).—The author considers the experiments of Sarthou (preceding abstract) indecisive, since the colorations obtained were due to the presence of casein, which is always present in milk filtered

* and *J. Pharm. Chim.*, 1910, [vii], **1**, 20—23.

through paper. When fresh or curdled milk is passed through the Chamberland filter, the filtrate gives no coloration with Storch's reagent. There is no evidence, therefore, of the presence of a soluble anæroxydase or insoluble catalase in cows' milk. W. O. W.

Can the Radium Emanations taken up by Drinking be Detected in the Urine? WALTHER LAQUER (*Chem. Zentr.*, 1909, ii, 854; from *Zeitsch. expt. Path. Ther.*, 1909, **6**, 868—878).—By the method employed, emanations of less than 20,000 units cannot be detected in urine. The quantity of emanation in urine increases with the quantity in the water drunk. All the values found must be multiplied by 2. The urine voided in the first half hour contains only three-quarters to four-fifths of the total excreted in the urine. The ratio of the quantity of emanation excreted to that ingested is about 1 : 4000. S. B. S.

The Origin of Ethereal Sulphates in the Organism. T. SATO (*Zeitsch. physiol. Chem.*, 1909, **63**, 378—396).—Rabbits were treated with phenol added to their diet (cabbage), and certain sulphur compounds also added. The nitrogen and sulphur (in various combinations) were estimated in the urine. Isethionic acid only slightly raises the output of ethereal sulphates, and has no effect on nitrogen. It appears to be rapidly excreted. Cystine raises the total sulphates, and the amount of ethereal sulphate is parallel to this. Albumose prepared from egg-albumin has no action. Sulphidal (a colloidal sulphur preparation) enormously increases both total and ethereal sulphate excretion. Thiocarbamide is largely excreted as such; the effect on the excretion of sulphates is doubtful; the urine does not show the reactions of thiosulphuric acid. W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. VI. The Excretion of Cholesterol by the Cat. G. W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, *B*, **81**, 505—515. Compare Abstr., 1909, ii, 595).—The tendency for the change of cholesterol of food to coprosterol in fæces appears to be greater in cats than in dogs. In experiments with two cats on a diet of sheep's brain, coprosterol free from cholesterol was recovered; on a meat diet the change was not complete; on vegetable diet and on an artificial diet, as free as possible from cholesterol or phytosterol, no fæcal coprosterol was found. A discussion of the part played by the cholesterols in the animal economy follows. G. S. W.

The Biological Significance of Lecithin. IV. The Blood-Content of Phosphorus and Iron in Lipoid Form in Cases of Polycythæmia rubra megalosplenica. W. GLIKIN (*Biochem. Zeitsch.*, 1909, **22**, 461—463. Compare Abstr., 1909, ii, 1038).—The lecithin content was found to be about 5 grams per 1000 c.c. in cases of this disease as compared with 2 to 3 grams per 1000 as found by Abderhalden in the blood of mammals normally. The phosphorus and total iron were also large as compared with that found in normal cases. S. B. S.

The Detection of Phosphorus and Hypophosphorous Acids in Organs after Phosphorus Poisoning. II. RICHARD EHRENFELD and WILHELM KULKA (*Zeitsch. physiol. Chem.*, 1909, **63**, 315—322. Compare Abstr., 1909, ii, 345).—Further investigations showed that during putrefactive processes the phosphorus is, in part, rapidly converted into phosphorous and hypophosphorous acids, but after this the change progresses but little. The experiments recorded further indicate that the normal phosphorised constituents of the body do not give rise to the acids mentioned. W. D. H.

***d*-Suprarenine (*d*-Adrenaline).** N. WATERMAN (*Zeitsch. physiol. Chem.*, 1909, **63**, 290—294).—Previous work on the superior physiological activity of *l*-adrenaline is confirmed; so also is Abderhalden's work on so-called adrenaline immunity. Administration of the *d*-compound increases the resistance of mice towards the *l*-variety. W. D. H.

The Antagonism between Adrenaline and the Chlorides of the Alkaline Earths and of Potassium. THEODOR FRANKL (*Pflüger's Archiv*, 1909, **130**, 346—352).—The action of adrenaline in stimulating sympathetic nerve-endings is antagonised by the chlorides mentioned in the title, of which the strongest is barium chloride. Sodium chloride has no such action. W. D. H.

Mode of Action of Nicotine and Curare, determined by the Form of the Contraction Curve and the Method of Temperature-coefficients. A. V. HILL (*J. Physiol.*, 1909, **39**, 361—373). —From a mathematical consideration of the curves of contraction and relaxation of muscles under the influence of curare and nicotine at different temperatures, the conclusion is drawn that there is a combination between the drug and some constituent of the muscle. Evidence is also adduced for the existence of two or more types of fibres (or contractions) in the muscle selected for experiment, the *rectus abdominis* of the frog. W. D. H.

Relative Toxicity of Various Salts and Acids towards Paramœcium. LORANDE LOSS WOODRUFF and HERBERT HORACE BUNZEL (*Amer. J. Physiol.*, 1909, **25**, 190—194).—The experiments with some exceptions indicate a marked parallelism between the order of toxicity of various cations and their ionic potential. The high migration velocity of hydrogen ions will explain their unexpectedly high toxicity. Specific affinities of the living cell for certain ions will explain other exceptional cases, for instance, the low toxicity of copper. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Degradation by Bacteria of the Ultimate Hydrolysis Products of Proteins. WALTHER BRASCH (*Biochem. Zeitsch.*, 1909, **22**, 403—406).—The degradation of various amino-acids by *Bacillus putrificus* and by mixed putrefying bacteria was investigated. Aspartic acid yields with mixed cultures propionic acid as chief product, together with small quantities of succinic acid. The pure culture gave the same products, together with small quantities of formic acid. Serine yielded both with pure and mixed cultures propionic acid with small quantities of formic acid. Tyrosine yielded with the pure culture *p*-hydroxyphenylpropionic acid. Glycine with the pure culture yielded acetic acid, alanine yielded propionic acid, and aminobutyric acid yielded butyric acid. S. B. S.

Accumulation of Nitrogen in Soils by Free Bacteria. ALFRED KOCH (*J. Landw.*, 1909, **57**, 269—286. Compare Abstr., 1908, ii, 56).—A continuation of the experiments made in 1905 and 1906 (*loc. cit.*) on the effect of sugar on fixation of nitrogen by *Azotobacter*. The results show a considerable after-effect, increased yields of buckwheat, oats, and wheat being obtained in 1907, 1908, and 1909, and that the increased yields diminish regularly each year.

Experiments with sand inoculated with soil showed a gain of 7·2 mg. N per 100 grams in four months when sugar was added; and vegetation experiments with buckwheat grown in sand showed a very greatly increased production of dry matter (98·1 grams) in presence of sugar as compared with the amount obtained without sugar (23·7 grams), whilst the amounts of nitrogen in the produce were 409 and 54 mg. respectively.

Further experiments in plots ($\frac{1}{2}$ square metre) with wheat, rye, and oats (in 1907, 1908, and 1909) showed that the nitrogen fixed in the first year was only utilised to a slight extent, whilst the yields were considerably increased in the second and third years.

The examination of fifteen different soils showed that *Azotobacter* was present in seven of them, whilst eight gave negative results. The latter included three light, sandy soils, peaty, light and heavy soils, and soil from a pine wood. Addition of sugar to three of these soils failed to produce an increase in the nitrogen content.

Experiments are described in which mannitol, dextrose, calcium succinate, glycerol, calcium butyrate (10 grams each), and xylan (5 grams) were added to soil (500 grams) which was kept for a month at 25°. The soil with mannitol and with dextrose gained 12·3 and 6·9 mg. nitrogen per 100 grams respectively, whilst the others lost nitrogen (0·8 to 5·3 mg.). N. H. J. M.

Production of Citric Acid by Citromyces. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1909, **23**, 830—833).—Citric acid is produced, not only when there is a deficiency of nitrogen, but also when any one of the

indispensable substances (phosphorus, potassium, iron or zinc, etc.) is absent or deficient. A mineral solution, in which iron or zinc is wanting, gives on addition of sucrose (10%) a very insignificant amount of growth. It will, however, produce in a few weeks relatively important amounts of citric acid.

The mechanism of the formation of citric acid is discussed (compare Buchner and Wüstenfeld, Abstr., 1909, ii, 602). N. H. J. M.

Fungi which Produce Citric Acid. CARL WEHMER (*Chem. Zeit.*, 1909, **33**, 1281).—In 1892 the author discovered two moulds which can convert sugar into citric acid (Abstr., 1893, ii, 591). Since then the number has been extended, and he has now isolated five or six others, morphologically much alike, capable of effecting the same change. *Citromyces Tollensianus* is characterised by its snow-white appearance in mass culture, although microscopically it differs but little from the others. Another species possesses the remarkable property of thriving in a saturated solution of oxalic acid (containing about 10% of acid); the hardiest mould previously known (*Aspergillus niger*) can only withstand about 1%, whilst most organisms are adversely affected by a trace. Another organism gives rise to oxalic instead of citric acid, but some oxalic acid (or rather its calcium salt) is always found in old cultures as a decomposition product of the citrate. E. J. R.

Theory of Disinfection. I. The Disinfecting Action of Phenol III. HEINRICH REICHEL (*Biochem. Zeitsch.*, 1909, **22**, 201—231. Compare Abstr, 1909, ii, 1045).—The assumption is made that the disinfecting action depends on the coefficient of distribution of the disinfectant between the two phases, namely, the bacteria and the disinfecting solution. The disinfecting action of phenol in the presence of varying quantities of sodium chloride was determined, suspensions of typhus bacilli and staphylococci being employed. The time of exposure to the solutions just necessary to kill the cultures was determined, the method of sub-culturing being employed. The curves obtained were submitted to mathematical analysis, and the factors influencing the distribution of the disinfectant between two phases, such as imbibition of water by the protein, etc., discussed. S. B. S.

Influence of Varying Relations between Lime and Magnesia on the Growth of Plants. LUIGI BERNADINI and A. SINISCALCHI (*Chem. Zentr.*, 1909, ii, 857; from *Staz. sper. agrar. ital.*, 1909, **42**, 369—386).—The injurious effect of an excess of calcium and the poisonous action of an excess of magnesium do not depend on the absolute amounts of calcium and magnesium ions taken up, but on the relation of the amounts absorbed by the plant to each other. The assimilated phosphoric acid is a function of the relation CaO/MgO in the nutritive medium, and depends on the relation of the calcium and magnesium ions in which these are absorbed. N. H. J. M.

Formation of Starch from Sorbitol in Rosaceæ. O. TREBOUX (*Ber. Deut. bot. Ges.*, 1909, **27**, 507—511).—Experiments with

numerous varieties of *Pomoideæ*, *Prunoideæ*, *Spiraeoideæ* showed that all of them are able to produce starch from sorbitol, whilst negative results were obtained with two other sub-orders, *Rosoideæ* and *Ruboideæ*, and with the related orders of the *Saxifraginæ* and *Leguminosæ*. None of the plants which produce starch from sorbitol are able to utilise mannitol and dulcitol.

As compared with sugars and glycerol, the production of starch from sorbitol is almost always much more vigorous.

Sorbitol has up to the present only been found in fruits, but further investigation will probably show that it occurs in leaves and other parts of plants. N. H. J. M.

Influence of Aluminium Salts on the Colour of Flowers VALENTIN VOUK (*Bied. Zentr.*, 1909, **38**, 755—756; from *Oesterr. bot. Zeitsch.*, 1909, **58**, 236—243).—Plants of *Hydrangea hortensis* watered with a 3% solution of alum produced flowers of a fine blue colour; at the same time brown spots appeared on the leaves, which died at an early stage. The best results were obtained with 1% solutions, which had no injurious effect, whilst the production of blue flowers was nearly complete. When aluminium sulphate was employed, the coloration was less strong.

Experiments with *Phlox decussata* gave negative results.

N. H. J. M.

Protective Action of Sodium for Plants. W. J. V. OSTERHOUT (*Bied. Zentr.*, 1909, **38**, 730—731; from *Jahrb. wiss. Bot.*, 1908, **46**, 121—136).—Water and soil culture experiments in which roots, algæ, and moulds, etc., were supplied with single salts and with mixtures showed that the poisonous action of calcium is diminished by addition of small amounts of a sodium salt. The antagonism between sodium and calcium salts is stronger than between sodium, magnesium, and potassium salts.

The conclusion is drawn that sodium is not a nutrient, but a protective, substance for plants, and probably for animals. Salts of aluminium, zinc, and cobalt have a protective action for animals, and salts of calcium for fungi. N. H. J. M.

Molecular Complexity of Caoutchouc in the Milk. F. WILLY HINRICHSEN and ERICH KINDSCHER (*Ber.*, 1909, **42**, 4329—4331).—The form in which caoutchouc occurs in the milk of caoutchouc-yielding plants is still unknown, Weber claiming that the milk contains a hydrocarbon, $C_{20}H_{32}$, which polymerises to caoutchouc during the technical preparation of the substance (Abstr., 1903, i, 845), whilst de Jong and Tromp de Haas (Abstr., 1904, ii, 762) assert that caoutchouc occurs already prepared in the milk; Harries also holds the latter view (Abstr., 1904, i, 1038). The authors have centrifugalised *Kickxia* milk with pure benzene until an approximately clear solution is obtained containing the caoutchouc and the caoutchouc-resin. The depression of the freezing point of this solution is determined; the residue is weighed after evaporation of the solvent, and extracted with acetone to remove the resin. The mole-

cular weight of the latter in benzene is 426, and by calculation the molecular weight of the caoutchouc is found to be 3173, a result which does not support Weber's view. C. S.

Influence of Anæsthetics and of Cold on Coumarin-producing Plants. ÉDOUARD HECKEL (*Compt. rend.*, 1909, **149**, 829—831. Compare Guignard, Abstr., 1909, ii, 823; Mirande, *ibid.*, ii, 824).—The odour of coumarin in plants, such as *Anthoxanthum odoratum* or *Melilotus officinalis*, is only perceptible in the dried leaf, but is rapidly developed in the living leaves when these are submitted to the action of anæsthetics or of cold. The author confirms the generality of similar phenomena observed by Guignard in the case of Cruciferæ, and has extended the experiments to *Lepidium latifolium* and *Cochlearia armoracia*. W. O. W.

Ajuga Iva. UGO PONTI (*Gazzetta*, 1909, **39**, ii, 349—353).—The plant *Ajuga Iva*, which is largely employed in the neighbourhood of Sassari as a remedy for malarial fever, contains no alkaloids, but, on distillation in a current of steam, yields a small quantity of a green oil having a characteristic aromatic odour. When treated with milk of lime, the herb yields ferulic acid, which probably exists in the plant in combination with phloroglucinol, thus:

$$OH\cdot C{<}\begin{matrix}C(OMe)\cdot CH\\ CH{=\!=\!=}CH\end{matrix}{>}C\cdot CH{:}CH\cdot CO\cdot C{<}\begin{matrix}C(OH)\cdot CH\\ C(OH){:}CH\end{matrix}{>}C\cdot OH,$$

this structure being analogous to that of homoeriodictyol (compare Power and Tutin, Trans., 1907, **91**, 887). T. H. P.

Presence of Aucubin in Different Varieties of Aucuba Japonica. C. LEBAS (*J. Pharm. Chim.*, 1909, [vi], **30**, 390—392).—Six garden varieties of this plant, namely, *elegantissima*, *latimaculata*, *longifolia*, *punctata*, *salicifolia*, and *viridis*, have been examined and found to contain aucubin (Bourquelot and Hérissey, Abstr., 1902, i, 634), which was isolated in the manner desciibed already (*loc. cit.*). The quantity obtained varied from 0·3% for *elegantissima* to 1·9% for *latimaculata*. T. A. H.

Occurrence of a Cyanogenetic Glucoside in Linaria Striata. ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1909, **30**, 385—389).—The plant was extracted with alcohol, and the concentrated extract dissolved as far as possible in an aqueous solution of thymol. This aqueous extract contained (1) sucrose, identified by its resolution into "invert sugar" by the action of invertase, and (2) a cyanogenetic glucoside, hydrolysed by emulsin into benzaldehyde, hydrogen cyanide, and a reducing sugar, probably dextrose. The amount of dextrose produced was in excess of that required for any known glucoside producing benzaldehyde, so that probably a second glucoside was present in the extract. T. A. H.

Existence of Two New Glucosides, Decomposable by a Ferment, in Primula officinalis. A. GORIS and MASCRÉ (*Compt. rend.*, 1909, **149**, 947—950).—The fresh roots of *Primula officinalis*,

like those of other species of *Primula*, emit a characteristic odour when bruised. This appears to be due to interaction between two glucosides and an enzyme, for which the name *primeverase* is suggested. The new ferment has been shown not to be identical with emulsin, myrosin, or betulase. Details are given of the method employed in isolating the glucosides, *primeverin* and *primulaverin*. The former occurs in colourless crystals, m. p. 172—173°, $[\alpha]_D - 60\cdot24°$, whilst the latter forms needles, m. p. 160—161°, $[\alpha]_D - 66\cdot86°$. Both are hydrolysed by dilute sulphuric acid, disengaging an odour of anise and furnishing a substance which, in the case of primeverin, develops a bright blue coloration with ferric chloride and a lilac-violet coloration in the case of primulaverin. W. O. W.

Localisation of Proteolytic Ferments in Vasconcellea quercifolia. The Rennet and Spontaneously Coagulable Latex. C. GERBER (*Compt. rend.*, 1909, **149**, 737—740. Compare Abstr., 1909, ii, 512, 824).—Unlike the majority of plants, the foliaceous ribs of *Vasconcellea quercifolia* show greater rennet activity than the parenchyma. Other parts of the plant show similar divergence from the general rule. This appears to be connected with the proportion of latex in the organs, since, for example, the ribs are richer in latex than the parenchyma. On the other hand, the presence of a milky latex, such as that of the chestnut, is not invariably associated with marked proteolytic activity. The rennet activity of *V. quercifolia*, *Funtumia elastica*, *Artocarpus incisa*, and *A. integrifolia* shows some proportionality to the readiness with which the sap undergoes spontaneous coagulation. W. O. W.

Action of Different Amounts of Copper in the Soil on the Growth of Plants. J. SIMON (*Landw. Versuchs.-Stat.*, 1909, **71**, 417—429).—Mustard and barley were grown in a mixed soil, in sand, in garden soil, and in a clay soil, to which small amounts of copper sulphate were added. In the mixed soil the yield of mustard was reduced by about 11—13% by 0·001 and 0·01% of copper sulphate and to 23 and 0·5% by 0·1 and 0·5% respectively, whilst the plants were killed by 1%. Barley is less sensitive, being unaffected by 0·001% of copper sulphate and remaining alive in presence of 1%. With regard to the sand and other soils, the experiments showed that copper sulphate is most poisonous in sand and least in the garden soil.

Experiments on the absorptive power of the soils showed that 100 grams of the garden soil absorbed 1·252 grams of copper sulphate, whilst the mixed soil and the clay soil absorbed 0·378 and 0·111 respectively, and the sand none at all. N. H. J. M.

Deposition of Nitrogen in Full-grown Animals with Abundant Food. KURT FRISKE (*Landw. Versuchs.-Stat.*, 1909, **71**, 440—482).—The results of the experiments of Lawes and Gilbert (*Phil. Trans.*, 1859, 493) on the changes in the composition of animals when fattened, showed that the gain is chiefly in fat (two-thirds) and water (one-fourth), and includes only a very small amount of nitrogenous matter. The experiments were made chiefly with young

animals. More recent experiments, with fully-grown animals, have also indicated, on the whole, that the gain in animals when fattened consists almost exclusively of fat.

In the experiments now described, eight full grown sheep (over four years old) were fed for six months on moderate amounts of hay. They were then shorn, weighed, and two of them killed and analysed. Two of them were then fed for about one hundred days on a nitrogenous diet of hay (450), beans (300), and sunflower cake (260 grams per day). The nutritive ratio was 1 : 2·88. Two others were fed with a less nitrogenous diet (1 : 5·02), consisting of hay (450), beans (270), and crushed barley (290 grams per day). The remaining two were reserve sheep which were not, however, required.

At the commencement, in the middle, and at the end of the fattening period, the sheep were kept for ten to eleven days in stalls for the collection of urine and fæces, which were weighed and analysed. Finally, the animals were again shorn, weighed, and then analysed.

The analytical results showed that, during fattening, the sheep put on considerable amounts of flesh, the greater gain being in the sheep with the nutritive ratio 1 : 5·02. The results of the balance experiments indicated a greater deposition of nitrogenous matter than the direct analysis.

The gain in fat was greater than the gain in flesh in both experiments. N. H. J. M.

Soil Analysis. JAMES HARVEY PETTIT (*J. Landw.*, 1909, **57**, 237—267; from *Inaug. Diss. Göttingen*, 1909).—The method of Schloesing and von Sigmond was employed with six different soils. The results showed very clearly a definite natural limit of solubility for phosphoric acid; and when the basicity of the soil is allowed for, the concentration of acid which acts uniformly lies between fairly definite limits, 400—800 mg. N_2O_5 per litre. The method also makes distinction between readily soluble and sparingly soluble potash, but a uniformly acting concentration was only found in the case of the loam.

The relation between the percentages of total phosphoric acid and total potash is not the same as the relation between the amounts soluble in dilute nitric acid. Muschechalk contains more total but much less readily soluble phosphoric acid than Buntsandstein.

The results of vegetation experiments agreed with the soil analyses in the case of loam and Muschechalk soils.

The amounts of phosphoric acid and potash assimilated by barley, beans, buckwheat, and potatoes are not the same as the amounts dissolved by dilute nitric acid. The different plants, moreover, take up very different amounts of these substances—buckwheat assimilated 3·5 times as much potash and twice as much phosphoric acid as barley; so that no one solvent can possibly indicate the amounts of nutritive substances available to all plants. It is therefore desirable to employ the term "readily soluble" instead of "available."

N. H. J M.

Analytical Chemistry.

Improved Method of Collecting Gases from the Mercury Pump. FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1909, **31**, 1271—1273).—In the ordinary method of collecting gases from the mercury pump in an inverted tube and transferring them to the gas analysis apparatus, minute bubbles of air are liable to be trapped even when great care is exercised. The following arrangement has been devised in order to avoid this source of error. A wide tube for collecting the gases is sealed on to the up-turned end of the capillary tube of the pump The wide tube is provided at the lower end with a side-tube, which is connected to a reservoir of mercury by means of rubber tubing. The upper end of the wide tube bears a three-way stopcock furnished with capillary leads. Towards the end of an ordinary exhaustion, the air in the wide tube can be expelled by raising the reservoir. On closing the stopcock and lowering the reservoir, a vacuum is formed in the tube, into which the bubbles passing down the pump capillary will be discharged. The method of employing the apparatus for the collection of gases is very simple, and is described with the aid of a diagram. E. G.

Automatic Filling Burette. R. FRAILONG (*Bull. Assoc. Chim. sucr. dist.*, 1909, **27**, 470—471).—A description of two kinds of automatic burettes, one intended to deliver a definite quantity of reagent at once, and the other for delivering the same drop by drop.

The main parts of the apparatus are a reservoir with a tube supplying the burette, a specially-constructed Mohr's pinchcock, which serves to open the outlet tube while closing simultaneously the supply tube, and a capillary tube passing through the rubber cork of the burette and dipping slightly into the liquid; it serves to obtain the zero point automatically. L. DE K.

Apparatus for the Rapid Electro-analytical Separation of Metals. HENRY J. S. SAND (*Trans. Faraday Soc.*, 1909, **5**, 159—164). —A description of some developments made in the author's apparatus for the rapid electro-analysis and separation of metals (compare Trans., 1907, **91**, 373; 1908, **93**, 1572).

A special screw-cap has been provided, which may be screwed down when the apparatus is not in use, making it possible to transport it without taking out the mercury which is employed to make connexion between the stationary and moving parts in the electrolytic stand. A clutch arrangement has also been added, which enables the operator to start or stop the rotation of the anode without stopping the motor.

All the apparatus required for the measurement of the electrode potential is now fitted into a single box. The arrangement is so designed that by depressing a key it will also allow the potential difference between the anode and the cathode to be read directly. The

capillary electrometer is retained as a zero instrument, and a special portable form, which is a modification of the Ostwald horizontal capillary electrometer, has been designed. It is provided with an enclosed scale, and will readily indicate one millivolt when observed with a lens. T. S. P.

Aluminium Dishes and other Appliances in Quantitative Analysis. JAROSLAV FORMÁNEK and FRANZ PEČ (*Chem. Zeit.*, 1909, **33**, 1282—1283).—Dishes of aluminium may be substituted for those of platinum in electrolytical separations, but it is necessary to have the inside of the dish plated with a very thin sheet of copper. This may then in turn be coated electrolytically with tin or silver, etc., according to circumstances. A number of successful experiments are communicated. Several improved appliances for quick electrolytic estimations are also described. L. DE K.

Electrolytic Estimation of Chlorine in Hydrochloric Acid with the Use of a Silver Anode. FRANK A. GOOCH and H. L. READ (*Amer. J. Sci.*, 1909, [iv], **28**, 544—552; *Zeitsch. anorg. Chem.*, 1909, **64**, 287—297).—The authors have shown by a large number of experiments that when using anodes of silver or silver-plated platinum gauze and currents of various strengths, the results are not so satisfactory as might have been expected. This is caused by the fixing of oxygen as well as chlorine on the anode, the removal of silver from the anode to the cathode, and the formation of hypochlorous acid. Even when the anode is ignited to decompose silver oxides, the results are still irregular and always low. L. DE K.

The Beilstein Reaction [for Halogens]. HUGO MILROTH (*Chem. Zeit.*, 1909, **33**, 1249).—The author has shown that the Beilstein copper oxide flame test for halogens is not absolutely trustworthy, as, owing to the formation of cupric cyanide, a green coloration is occasionally noticed, which, although not quite so characteristic, may be mistaken for the halogen colour.

The reaction is given by picolinic acid, quinolinic acid, 2-methylpicolinic acid, dipicolinic acid, methyl 2-hydroxynicotinate, quinaldinic acid, and nicotinic acid, whereas no green flame was observed with quinoline, *iso*quinoline, *iso*nicotinic acid, cinchoninic acid, cinchomeronic acid, methylanthranilic acid, apophylenic acid, and papaveric acid.

In the case of hydroxyquinoline the reaction is obtained even without the use of a copper oxide bead. L. DE K.

Analysis of Mixtures of Halogen Acids. II. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1909, **31**, 1273—1275. Compare Abstr., 1909, ii, 612).—The following method is recommended for the analysis of mixtures containing two halide ions. Silver nitrate is added in excess, and the precipitated silver salts are collected and weighed. The solution containing the excess of silver nitrate is titrated with thiocyanate and ferric nitrate by the Volhard method. It is shown that if a is the weight of silver nitrate required to precipitate both the halogens present, and b is the weight of silver

halides precipitated, the quantities of the halogens can be calculated by the following equations. For mixtures containing chlorine and bromine: $Cl = 0{\cdot}8817a - 0{\cdot}7976b$; $Br = 1{\cdot}7976b - 1{\cdot}5166a$. For mixtures containing chlorine and iodine: $Cl = 0{\cdot}5358a - 0{\cdot}3877b$; $I = 1{\cdot}3877b - 1{\cdot}1706a$. For mixtures containing bromine and iodine: $Br = 2{\cdot}3501a - 1{\cdot}7004b$; $I = 2{\cdot}7007b - 2{\cdot}9851a$.

Mixtures containing three halide ions can be analysed by the same method if one of the halogens is estimated separately. Thus, if iodine is estimated separately, we have $Cl = 0{\cdot}8817a - 0{\cdot}7976b$ $(+0{\cdot}2954\ I)$; $Br = 1{\cdot}7976b - 1{\cdot}5166a$ $(-1{\cdot}2951\ I)$. If the bromine is estimated separately, $Cl = 0{\cdot}5358a - 0{\cdot}3877b$ $(-0{\cdot}2280\ Br)$; $I = 1{\cdot}3877b - 1{\cdot}1706a$ $(0{\cdot}7720\ Br)$. If the chlorine is estimated separately, $Br = 2{\cdot}3501a - 1{\cdot}7004b$ $(-0{\cdot}4386\ Cl)$; $I = 2{\cdot}7007b - 2{\cdot}9851a$ $(+3{\cdot}3857\ Cl)$. E. G.

Estimation of Perchlorates by means of Titanous Salts. VICTOR ROTHMUND and A. BURGSTALLER (*Chem. Zeit.*, 1909, **33**, 1245).—Contrary to Stahler's statement (Abstr., 1909, ii, 699) that the estimation of perchloric acid by boiling with excess of titanous sulphate and then titrating with permanganate is unsatisfactory, the authors find that the results are trustworthy, provided the operation takes place in a flask fitted with a cooling arrangement, and in an atmosphere of carbon dioxide.

The chloride formed in the reaction may be estimated by way of a check, but the use of the nephelometer cannot be recommended in this case. L. DE K.

Simple Process for the Estimation of Iodine. ERNST WINTERSTEIN and E. HERZFELD (*Zeitsch. physiol. Chem.*, 1909, **63**, 49—57).—The apparatus consists of a 250 c.c. round-bottomed flask with a narrow neck, which is closed by means of a ground joint, through which pass two tubes, like those of an ordinary washbottle. The exit tube is also furnished with a ground joint, by means of which it is connected with a short condenser. The end of the condensing tube is connected with two absorption flasks filled half way with a 10% solution of potassium iodide.

Fifty c.c. of the solution to be tested for small quantities of iodides (bromides or chlorides do not interfere) are placed in the flask, together with 5 c.c. of phosphoric acid and 10—20 c.c. of commercial hydrogen peroxide. A current of air is drawn through the apparatus, and the solution is heated gradually to boiling. After thirty minutes the iodine is expelled and absorbed by the potassium iodide, and may be titrated.

When applying the process to urine, the results are only qualitative, but the full amount of iodine present may be obtained by rendering the urine alkaline with sodium hydroxide, evaporating to dryness, and destroying the iodised organic compounds by ignition. L. DE K.

Estimation of Iodine in Organic Substances. VINCENZO PAOLINI (*Mon. Sci.*, 1909, [iv], **23**, 648).—The following method is recommended for the estimation of iodine in such substances as blood,

urine, brain-substance, sea-weed, thyroid glands, etc. A particular instance is given of the estimation of iodine in iodoform-gauze. Ten grams of the gauze, cut into small pieces, are treated in a flask with 40 grams of zinc dust and 60 c.c. of 25% sulphuric acid. The mixture is heated by means of a water-bath in a reflux apparatus for about three hours, a further 50 c.c. of sulphuric acid being then added and the heating continued for some hours. The iodine present is thus converted into hydriodic acid. The gauze is then washed several times by decantation with water, and the solution made up to a volume of 1 litre. One hundred c.c. of this solution are treated with a few c.c. of potassium nitrite solution and extracted with 100 c.c. of carbon disulphide. The carbon disulphide is then separated, washed with water, and the iodine dissolved in it is titrated with standard thiosulphate solution in the presence of sodium hydrogen carbonate.

W. P. S.

Estimation of Iodine in the Thyroid. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1909, **31**, 1326—1329).—Riggs (Abstr., 1909, ii, 699) has stated that the estimation of iodine in the thyroid by Baumann's method (Abstr., 1896, ii, 487) is liable to error, owing to the formation of iodate during the fusion, and he has therefore suggested a modification involving a reduction process.

In the present paper, an account is given of experiments which indicate that Baumann's method is satisfactory, and that Riggs' modification is not only unnecessary, but actually leads to greater error than the original method, since it is difficult to remove the whole of the iodine from the aqueous layer before applying the reduction process, and any iodine remaining in solution renders the results inaccurate.

E. G.

Estimation of Sulphur Dioxide and Sulphuric Acid in the Gases of Sulphur Furnaces. HENRI PELLET (*Bull. Assoc. Chim. sucr. dist.*, 1909, **27**, 468—469).—The author described his sulphicarbonimeter some ten years ago in a pamphlet issued for private circulation, and now communicates some results obtained. The process is based on the fact that on passing the gases through water, the sulphuric acid is removed, the sulphur dioxide being absorbed by a suitable reagent contained in a second washbottle.

L. DE K.

Estimation of Dithionic Acid and Dithionates. HENRI BAUBIGNY (*Compt. rend.*, 1909, **149**, 1069—1071. Compare Ashley, Abstr., 1906, ii, 800).—Preliminary experiments showed that it was not possible to oxidise dithionic acid completely to sulphuric acid by heating with *aqua regia*, either in open or closed vessels.

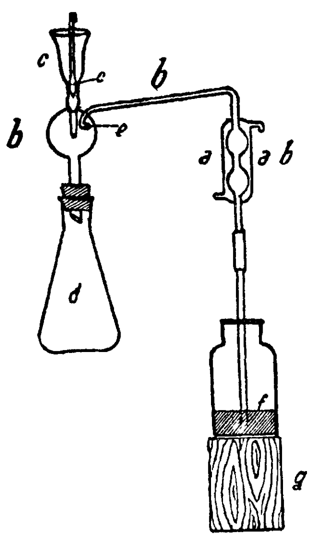
The solution containing the dithionate is mixed with a sufficient amount (12 to 15 times the quantity of dithionate present) of a mixture of sodium carbonate and nitrate. If a precipitate is formed, it is filtered off and washed; the filtrate and washings are then evaporated to dryness, and the residue carefully fused during from ten to fifteen minutes. The sodium sulphate so formed is estimated in the usual way with barium nitrate in presence of nitric acid.

T. A. H.

Estimation of Nitrogen in Soil Extracts. DENSCH (*Chem. Zeit.*, 1909, 33, 1249—1251).—A reply to Mitscherlich (Abstr., 1909, ii, 935).—The author upholds the accuracy of his process, and prefers it to the more scientific method of Mitscherlich in the case of analysis of the aqueous extract of soils. For the reduction of the nitrates (any nitrite is first oxidised by means of permanganate) in acid solution, a mixture of iron and zinc powder is recommended, although iron alone may be used. L. DE K.

Method of Estimating very Small Amounts of Nitrogen. T. ZELLER (*Landw. Versuchs.-Stat.*, 1909, 71, 437—440).—The method described by Mitscherlich, Herz, and Merres (Abstr., 1909, ii, 614) is considered impracticable, owing to the relatively large and variable amounts of nitrogen unavoidably introduced in the reagents. N. H. J. M.

New Distillation Arrangement for Ammonia Estimation. ADOLF BERTHOLD (*Chem. Zeit.*, 1909, 33, 1292).—By using this apparatus all loss of ammonia is avoided.



The substance is placed in the flask *d*, and the centre-piece *b* is put on. The receiver *f*, which contains the standard acid, is then raised by a wooden block *g* until the delivery tube dips into the acid. The funnel *c* is now filled with alkali, and by gently lifting the tube *e* the liquid is allowed to run into *d*, but a little should be left in the funnel so as to form a seal; the remaining alkali is then removed by rinsing a few times with water still retaining the seal. After connecting the condenser *a* with the water supply, the contents of *d* are heated over a Bunsen burner. When the distillation is practically finished, the wooden block is removed and the distillation continued for a short time.

When dealing with liquids containing free ammonia, these should be introduced through the funnel tube *c* after placing on the centre-piece and raising the receiver. Into *e* a drop catcher has been sealed. L. DE K.

Estimation of very Small Amounts of Ammonia in Large Quantities of Air. PAUL LIECHTI and ERNST RITTER (*Chem. Zeit.*, 1909, 33, 1265—1266).—The apparatus consists of a U-tube containing diluted *N*-sulphuric acid, one limb of which is attached to a vertical, spindle-shaped tube, which is connected to the first of two pipettes inclined at about 45° to the vertical; the top pipette is attached to a second U-tube. By means of a ventilating fan, the air is drawn very rapidly through the apparatus. The acid is swept

mainly into the spindle-shaped tube, where it is churned violently by the air current, and a good deal of the acid is converted into spray; this, however, settles on the walls of the two pipettes and flows back; it is found that practically every trace of ammonia is removed.

L. DE K.

New Arrangement for the Estimation of Nitric Compounds in Sulphuric Acid. K. LEO (*Chem. Zeit.*, 1909, **33**, 1218—1220).—Instead of shaking the sulphuric acid with mercury (Lunge's process), 50 c.c. of the sample are placed in a specially constructed bulb, the remaining space being taken up with mercury. By means of a tube furnished with three openings and connected with a mercury pressure flask, mercury is forced into the acid like a spray, and the action soon starts. The mercury displaced runs into another reservoir, and from there into a beaker, and is afterwards emptied into the pressure flask. The nitric oxide liberated is then transferred to a gas volumeter and measured.

For working details the illustrations in the original article should be consulted.

L. DE K.

Reduction of Nitric Nitrogen to Ammonia; New Process for the Estimation of Nitrates. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim sucr. dist.*, 1909, **27**, 457—459; *Ann. Chim. anal.*, 1909, **14**, 445—446).—The nitrate is placed in a distilling flask fitted with a funnel safety tube, 5 to 6 grams of aluminium cuttings and 2 c.c. of a saturated solution of mercuric chloride are added, and also 150 to 200 c.c. of water. After connecting the flask with the condensing apparatus, a brisk evolution of hydrogen will be noticed; a solution of sodium hydroxide is added, and the ammonia formed is distilled off and collected as usual in standard acid. In order to decompose traces of ammoniated mercury compounds, a few c.c. of sodium hypophosphite solution are added towards the end.

L. DE K.

Modification of the Grandval and Lajoux Process for the Estimation of Nitrates in Waters Charged with Chlorides. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], **5**, 1088—1090).—The author stated previously that in the presence of chlorides the process used by Grandval and Lajoux failed to give correct results, and he constructed correction tables. By operating as follows, and using an improved reagent, the use of these tables may be avoided.

One volume of a mixture of 37 parts of sulphuric acid and 3 parts of phenol is mixed with 1 volume and a-half of hydrochloric acid and 1 volume and a-half of water, and heated for half an hour on the water-bath. The residue left on evaporation of the sample is moistened with 1 c.c. of the reagent and heated on the water-bath for fifteen minutes. The residue is then rendered alkaline with ammonia, and the coloration compared with that of a standard water similarly treated.

L. DE K.

Influence of Nitrites on the Estimation of Nitrates by Grandval and Lajoux's Process. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], **5**, 1090—1091).—The author states that, although nitrites do not themselves affect Grandval and Lajoux's reagent, the least trace of nitrate added gives a coloration far more powerful than would be expected.

The nitrite should therefore be estimated separately by means of Griess' reagent, and before estimating the nitrate it should be oxidised with permanganate, or else destroyed by means of carbamide.

L. DE K.

Influence of Chlorides on the Estimation of Nitrates. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], **5**, 1091).—The loss in nitrate observed when applying the Grandval and Lajoux colorimetric test for nitrates in presence of chlorine is due to the formation of nitro-hydrochloric acid; this may be proved by passing the gaseous products of the reaction through a solution of potassium iodide, when the amount of iodine liberated corresponds with the loss observed.

A slight mechanical loss owing to effervescence is also unavoidable.

L. DE K.

Coloured Substances Produced in Grandval and Lajoux's Reaction. MAURICE LOMBARD (*Bull. Soc. chim.*, 1909, [iv], **5**, 1092—1096).—The coloration is mainly caused by a mixture of *o*-nitrophenol-*p*-sulphonic acid and *o*-nitrophenol. The latter substance gives a more intense red coloration with ammonia. L. DE K.

Estimation of Mineral Constituents in Vegetable Substances. L. VUAFLART (*Bull. Assoc Chim. sucr. dist*, 1909, **27**, 454—456).—Polemical. A reply to Pellet (Abstr., 1909, ii, 755) on the subject of the volatilisation of phosphoric compounds on incinerating vegetable substances. The errors are avoided by using the moist combustion process with sulphuric acid. The use of alcohol when estimating nitrates is also discussed, also the possibility of some magnesium ammonium phosphate remaining on the filter when dissolving the yellow molybdate precipitate in dilute ammonia containing some citrate solution. L. DE K.

Estimation of Mineral Constituents in Vegetable Substances. HENRI PELLET (*Bull. Assoc. Chim. sucr. dist.*, 1909, **27**, 456—457).—Polemical. A further reply to Vuaflart (preceding abstract). The author did use citrate solution, and not nitrate, as reported erroneously. Attention is called to the fact that the application of alcohol in the estimation of nitrates has already been advocated by Boussingault in 1865. L. DE K.

Estimation of the Free Acid in Superphosphates. FREDERICK B. GUTHRIE and A. ALEXANDER RAMSAY (*J. Roy. Soc. New South Wales*, 1909, **43**, 69—74).—The methods recommended for the estimation of free phosphoric acid have been examined. Herzfelder's method, in which the free acid is extracted with ether and titrated in aqueous solution with methyl-orange as indicator, gives the best results, but

the values obtained are rather low. A modification of this method, in which sodium alizarinsulphonate is used as indicator, will probably prove to be the best method of estimating free phosphoric acid in superphosphates. H. M. D.

Estimation of Total Phosphoric Acid in Basic Slags and Native Phosphates by the "Citro-mechanic Method." E. GUERRY and E. TOUSSAINT (*Bull. Soc. chim. Belg.*, 1909, **23**, 454—457).—Twenty to twenty-five c.c. of sulphuric acid are introduced into a 250 c.c. Jena flask by means of a funnel tube so as not to moisten the neck. 2·5 Grams of the powdered sample are added, and, after gently shaking, the whole is boiled for ten minutes. When cold, water is added a little at a time, and when cooled down, the solution is diluted to the mark, well shaken, and filtered. Twenty-five c.c. of the filtrate are placed in a beaker and neutralised with ammonia, and when cold, 30 c.c. of ammonium citrate solution (= 10 grams of citric acid) are added, followed by 15 c.c. of ammonia. After starting the stirring machine, 35 c.c. of magnesium mixture are added drop by drop, and, after twenty-five minutes, the precipitate is collected, washed with dilute ammonia, and ignited.

No correction need be made for the volume of the insoluble matter, as this contains relatively the same amount of phosphoric acid as the solution. L. DE K.

Estimation of Hypophosphoric, Phosphorous, and Hypophosphorous Acids in Presence of One Another, and of Phosphoric Acid. ARTHUR ROSENHEIM and JAKOB PINSKER (*Zeitsch. anorg. Chem.*, 1909, **64**, 327—341).—A method was required for the analysis of the acid obtained from the action of moist air on yellow phosphorus.

Hypophosphoric acid (the pure sodium salt was used) may be estimated by titration with permanganate if certain precautions are observed. The slightly acid solution, with the addition of a small quantity of permanganate, is heated to 80—90°, titrated rapidly with oxalic acid, more permanganate added, and so on, until a red coloration persisting for five minutes is obtained. The excess is then titrated with oxalic acid:

$$10H_2PO_3 + 2KMnO_4 + 3H_2SO_4 + 2H_2O = 10H_3PO_4 + 2MnSO_4 + K_2SO_4.$$

Iodine is without action on hypophosphoric acid. Uranyl salts give a yellow precipitate according to the equation: $2NaHPO_3 + UO_2(NO_3)_2 = UO_2(HPO_3)_2 + 2NaNO_3$.

Phosphorous acid may be estimated by means of permanganate under the same conditions as hypophosphoric acid. It reacts quantitatively with iodine, when heated in a closed flask, to form phosphoric acid, and may thus be estimated in the presence of hypophosphoric acid.

Hypophosphorous acid may be titrated with permanganate as above:

$$5H_3PO_2 + 4KMnO_4 + 6H_2SO_4 = 5H_3PO_4 + 4MnSO_4 + 6H_2O + 2K_2SO_4,$$

and also reacts quantitatively with iodine when heated in acid solution in a closed flask. In all cases the oxidation of any one acid is unaffected by the presence of one or more of the other acids. A.

mixture containing phosphoric, phosphorous, hypophosphoric, and hypophosphorous acids may be analysed by (1) oxidising with nitric acid and precipitating with magnesia, thus estimating total phosphorous; (2) titrating with permanganate, which oxidises all but the phosphoric acid; (3) titrating with iodine, which oxidises only phosphorous and hypophosphorous acids; (4) titrating with uranyl nitrate, which precipitates only phosphoric and hypophosphoric acids. Equations for calculating the proportions are given.

An application of this method of analysis to the product obtained by the oxidation of phosphorus in moist air at 5°, shows that the solution contains principally hypophosphoric acid. C. H. D.

Apparatus for the Estimation of Carbon Dioxide in Milk. A. Barillé (*J. Pharm. Chim.*, 1909, [vi], **30**, 452—453).—The apparatus, which is figured in the original, consists of a flask connected with (1) washbottles containing potassium hydroxide solution through which air freed from carbon dioxide may be introduced at will, and (2) washbottles containing ammoniacal baryta water for the absorption of the carbon dioxide liberated. Eight hundred c.c. of milk are introduced into the flask, heated at 50°, and the last traces of carbon dioxide swept by a current of purified air into the baryta solution, where it is estimated. The "combined" carbon dioxide is then estimated by adding excess of tartaric acid to the milk and proceeding as before. The apparatus gives results within 1% of the theoretical.

T. A. H.

Estimation of Potassium in Potassium Silicates. Aart Verwey (*Zeitsch. anal. Chem.*, 1909, **48**, 760—762).—A slight modification of Lawrence Smith's well-known method. One gram of the finely-powdered silicate is intimately mixed with 1 gram of pure ammonium chloride and 5 grams of alkali-free calcium carbonate, and the whole is introduced into a platinum crucible 4·5 cm. in height and 3·5 cm. in width. After covering the mixture with a layer of 3 grams of calcium carbonate, the crucible is heated until the ammonia is expelled, and, after putting the lid on, a strong heat is applied for an hour with a Teclu or a powerful Bunsen burner.

The mass is then boiled with water for fifteen minutes, and, when cold, the liquid is made up to 200 c.c., and in 50 or 100 c.c. of the filtrate the potassium is estimated by acidifying with hydrochloric acid and evaporating with excess of platinic chloride as usual.

L. de K.

Estimation of Zinc and Analysis of Zinc Ores. K. Voigt (*Zeitsch. angew. Chem.*, 1909, **22**, 2280—2285).—Complete analyses are given of a few zinc ores by known methods. The author prefers precipitating the zinc as zinc ammonium phosphate after removing any calcium with ammonium carbonate in ammoniacal solution. Sulphur is best estimated after a preliminary fusion with a mixture of 5 parts of anhydrous sodium carbonate and 3 parts of potassium chlorate. If the ore contains an appreciable amount of matter

insoluble in acid, this should be fused with sodium carbonate and then again treated with hydrochloric acid. L. DE K.

The Most Rapid Wet Lead Assay. JULIUS F. SACHER (*Chem. Zeit.*, 1909, **33**, 1257—1258).—A slight modification of Alexander's process (separation of lead as sulphate, dissolution in ammonium acetate, and titration of the slightly acidified solution with standardised ammonium molybdate with tannin as external indicator).

The author finds the previous separation of the lead as sulphate unnecessary, and titrates the nitric acid solution at once after adding first a sufficiency of ammonia and then an excess of acetic acid.

Supposing 1 c.c. of the molybdate solution = 0·01 gram of lead, a correction must be made depending on the final volume of the liquid. For 50 c.c., 0·18 c.c. of molybdate should be deducted; for 100 c.c., 0·3 c.c.; for 125 c.c., 0·40 c.c.; for 150 c.c., 0·45 c.c.; for 175 c.c., 0·50 c.c.; for 200 c.c., 0·54 c.c.; for 250 c.c., 0·60 c.c.; and for 300 c.c. of liquid, 0·75 c.c. of molybdate solution.

If iron is present to any extent, it should be removed from the solution by heating this for some time on the water-bath.

L. DE K.

Detection of Mercury in Urine. WILH. BECKER (*Pharm. Zeit.*, 1909, **54**, 987).—Polemical. A reply to Stich (Abstr., 1909, ii, 1055). The method given by Almén only yields approximate results, but the processes communicated by Farup and by Schumacher-Jung allow the determination of 0·1 mg. of mercury in urine. Bunge's balances, provided with a glass micrometer and indicating 1/20 mg., are recommended. L. DE K.

Detection of Mercury in Urine. FRITZ GLASER and A. ISENBURG (*Chem. Zeit.*, 1909, **33**, 1258).—To 250 c.c. of the sample are added 5 grams of pure aluminium sulphate, and the solution is heated and precipitated with ammonia. The precipitate is then collected, dissolved in hydrochloric acid, and heated on the water-bath for forty-five minutes in presence of a copper spiral. The deposit is then, as usual, sublimed and converted into the red iodide. L. DE K.

Electro-analysis of Mercury Compounds with a Gold Cathode. F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1909, **5**, 45—48).—Using a gold flag electrode, a large number of estimations of mercury were made, using mercuric chloride, bromide, and sulphate. The electrolytes employed were nitric acid, sulphuric acid, potassium cyanide and sodium sulphide. The results obtained were always high—from 0·5 to 2·5%. This was at first attributed to occluded hydrogen, but it was not found that the gold electrode increased in weight when made the cathode in dilute sulphuric acid and the current passed for twenty hours. When the electrode coated with mercury was treated in a similar manner, it also showed no increase in weight. Since the electrode was cathode, the increase in weight could not be due to oxidation, and when a platinum electrode was run in series with it, the mercury deposited on the platinum was always slightly less than

that theoretically required. The author cannot explain the results, which show, however, that a gold electrode cannot be satisfactorily used for analytical purposes.

A rotating silver electrode showed similar results to the gold electrode. Usually the time required to deposit the mercury was from five to six hours, but on stirring the electrolyte by means of a powerful magnetic field, the time of deposition was reduced to fifty minutes; the results were still too high.

The author comes to the conclusion that the best electrode on which to deposit mercury is one of mercury, the deposition being very rapid if a rotating anode is used (compare Smith and Kolloch, Abstr., 1905, ii, 859; 1906, ii, 194). Two quartz vessels, one of them fitted with a siphon side tube, are described for use with a mercury cathode.

T. S. P.

Estimation of Manganese by Volhard and Wolff's Method. WALDEMAR M. FISCHER (*Zeitsch. anal. Chem.*, 1909, **48**, 751—760).—A slight modification of the Volhard-Wolff permanganate titration process. The sulphuric or hydrochloric acid solution (containing about 0·35 gram of manganese) is diluted to 500 c.c., and aqueous sodium hydroxide is added until a slight precipitate forms, which is then at once redissolved by a few drops of dilute sulphuric acid. One gram of freshly ignited zinc oxide and 10 grams of zinc sulphate are added, and, after heating the solution to boiling, it is titrated with $N/10$ permanganate. One c.c. of pure glacial acetic acid is added, and the liquid is again heated to boiling. This causes the precipitate to coagulate and to settle rapidly, and the pink coloration to disappear; the titration is then continued until the pink colour is restored.

L. DE K.

Separation of Manganese and Chromium. FERDINAND FALCO (*Arch. Pharm.*, 1909, **247**, 431—436).—A modification of Kassner's process, by means of which good results are obtained when the amount of manganese does not exceed 0·015 gram.

The solution is placed in a covered beaker, and sodium peroxide added in small portions. The liquid is then heated until the precipitate has separated in brown flocks. The liquid is decanted through a filter, and the precipitate washed with boiling water, and finally collected on the filter; the filtrate contains the chromium as chromate. The manganese peroxide is dissolved off the filter by means of hot 20% hydrochloric acid, and returned to the beaker. Excess of bromine water is added, followed by an excess of ammonia, and the liquid is heated to boiling. The precipitate is then collected, washed, ignited, and weighed as manganosomanganic oxide. The filtrate, which may still contain traces of chromium, is added to the main solution.

L. DE K.

Quantitative Separations by Means of Ammonium "Cupferron" (Nitrosophenylhydroxylamine). OSCAR BAUDISCH (*Chem. Zeit.*, 1909, **33**, 1298—1300).—*Analysis of Brown Iron Ore.*—Five grams of the ore are dissolved in 60 c.c. of strong hydrochloric acid; the

iron is fully oxidised by boiling with potassium chlorate, and, when cold, the whole is diluted to 500 c.c. Twenty-five c.c. of the liquid are placed in a beaker, and 20 c.c. of hydrochloric acid and 100 c.c. of cold distilled water are added. While stirring, a solution of 3 grams of "cupferron" in 50 c.c. of water is added. The iron is completely precipitated when a white precipitate begins to form. The precipitate is now collected, and washed with cold water until the washings are no longer acid; the filtrate is used for the estimation of manganese. The filter is then washed with dilute ammonia (1 : 1) to remove the excess of "cupferron," and the precipitate is then washed once with water, and finally converted by ignition into oxide and weighed as such.

Analysis of Nickel Ore.—The iron and copper present are precipitated jointly with "cupferron," and in the filtrate the nickel is estimated by a suitable method. The copper is extracted from the washed precipitate with strong ammonia, and the copper is then obtained as oxide by evaporating the solution and igniting the residue; the oxide may be reduced to metal, and weighed as such. The precipitate insoluble in ammonia is then ignited and weighed as ferric oxide.

The use of "cupferron" in a number of other cases is suggested.

L. DE K.

Rapid Electrolytic Estimation of Cobalt. PIERRE BRUYLANTS (*Bull. Soc. chim. Belg.*, 1909, **23**, 383—400).—A lengthy paper containing a large number of experiments recorded in sixteen tables. The electrolytic estimation of cobalt in ammoniacal solution gives good results with a cathodic potential of 1·35 volts. If the same process as for the rapid estimation of nickel is applied, a spongy and partly oxidised metallic deposit is obtained. In any case the metal is very readily oxidised and redissolved, so that it must be washed without interrupting the current. Under proper conditions cobalt may, like lead and manganese, be deposited as peroxide at the anode. Electrolysis from an oxalic acid solution cannot be recommended, as the deposit then contains carbon.

An approximate separation of cobalt from zinc may be obtained when operating in ammoniacal solution as directed above. If sodium sulphite is also added, the cobalt, although free from zinc, contains an appreciable amount of sulphur.

L. DE K.

Gravimetric Estimation of Chromium; Quantitative Hydrolysis of Sesquioxides. WALTER SCHOELLER and WALTER SCHRAUTH (*Chem. Zeit.*, 1909, **33**, 1237).—The neutralised solution of the chromic salt, which contains 0·1—0·2 gram of metal, and is diluted to about 300 c.c., is heated to boiling, and 3 c.c. of aniline are added in portions of 1 c.c. After boiling for five minutes, the chromium has been precipitated quantitatively as hydroxide in a form which may be readily washed by decantation.

The process may be used in the presence of manganous salts. Salts of aluminium, zinc, and ferric iron are also precipitated by aniline, but whether the process is sufficiently accurate for these metals has not, as yet, been decided.

L. DE K.

Estimation of Titanic Acid in Ilmenite. ELISE RÖER (*Chem. Zeit.*, 1909, **33**, 1225—1226).—0·5 Gram of the finely-powdered ore is heated with 10 grams of anhydrous sodium carbonate, finally over the blowpipe for half an hour. The liquid mass is poured into a platinum dish placed in cold water, and when cold it is put together with the crucible into a spacious beaker containing 50 c.c. of cold water. The portion left undissolved is washed on a filter, then transferred to an Erlenmeyer flask of one litre capacity, and heated with dilute hydrochloric or sulphuric acid until quite dissolved.

When cold, the solution is rendered slightly alkaline with sodium hydroxide, and then again slightly acidified with sulphuric acid. One hundred c.c. of strong sulphur dioxide solution are added, and enough water to obtain a volume of 700 c.c. The whole is now boiled on an asbestos plate for one hour, and another 20 c.c. of sulphur dioxide solution are added. After remaining for a few hours in a slanting position, the precipitate is collected, washed with boiling water, ignited, and weighed as titanium peroxide. L. DE K.

Estimation of Thorium in Monazite. Colorimetric Estimation of Small Amounts of Platinum. JOHN C. H. MINGAYE (*Records Geol. Survey N. S. Wales*, 1909, **8**, 276—286).—*Estimation of Thorium in Monazite.*—Samples of Carolina monazite have been analysed by several methods. The precipitate obtained with sodium thiosulphate must be redissolved, precipitated with oxalic acid, and extracted with ammonium oxalate. Precipitation with moist lead carbonate (Giles, Abstr., 1905, ii, 615) gives good results if the precipitation is repeated. Precipitation as basic acetate (Haber, Abstr., 1898, ii, 295) is rapid and sufficiently accurate. Several Australian monazites have also been examined, the richest being a sand from Black Swamp, Torrington, New South Wales, containing 4·12% of thoria.

Colorimetric Estimation of Platinum.—The small quantities of platinum occurring in beach sands or alluvial deposits may be estimated by fluxing with litharge and charcoal to obtain a lead button, cupelling with the addition of silver, and parting with nitric acid, D 1·28, which dissolves platinum and silver, leaving gold and iridosmine. The silver is precipitated as chloride, and the filtrate evaporated twice to dryness with hydrochloric acid. The hydrochloric acid solution, filtered from traces of lead and silver chlorides, is treated with stannous chloride or potassium iodide, and the coloration obtained compared with that of a standard solution containing 0·065 gram platinum per litre. Quantities of platinum as small as 0·06 gram per ton may be estimated in this way. C. H. D.

Methods for the Quantitative Chemical Analysis of Animal Tissues. I. General Principles. WALDEMAR KOCH (*J. Amer. Chem. Soc.*, 1909, **31**, 1329—1335).—A discussion of the general principles on which accurate methods of analysis of animal tissues depend and of the manner in which the analytical data should be applied in order to yield results of value to the physiologist. The difficulties attending such work are pointed out. It is suggested that the constituents of the cell may be conveniently arranged in the

following classes: (1) lipoids, including phosphatides, cerebrins, and cholesterol; (2) extractives, such as creatine, taurine, and hypoxanthine; (3) inorganic constituents, represented by the ash; (4) proteins; (5) fats; (6) carbohydrates, namely, glycogen. Very few of the methods at present employed for estimating these various groups are at all satisfactory, and it is therefore considered more useful to study the distribution of the three elements, nitrogen, phosphorus, and sulphur, which are of special interest, as they are involved in somewhat different phases of cell activity. From a physiological standpoint, it is desirable to study the same tissue under different conditions, of which the three most important are: (1) the period of growth or development; (2) conditions of pathological change; and (3) conditions of starvation, the first of these being the most favourable for a study of the chemical transformations in the cell.

As an illustration, analyses are given of (1) a very young brain, (2) an adult brain, and (3) a brain from a case of dementia præcox. The young brain contained a larger quantity of extractives than the adult brain, whilst the latter contained a greater proportion of lipoids. The brain from the case of dementia præcox resembled the normal brain, but contained a smaller quantity of partly oxidised sulphur compounds, soluble in water. E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. II. Collection and Preservation of Material. WALDEMAR KOCH and SIDNEY A. MANN (*J. Amer. Chem. Soc.*, 1909, 31, 1335—1341. Compare preceding abstract).—An account is given of the precautions to be observed in order to obtain uniform and representative samples for analysis, and of the methods of preserving the material. The chief methods of preservation are (1) immersion in alcohol, (2) drying, and (3) the addition of a dehydrating agent, such as sodium sulphate or gypsum. The relative advantages and disadvantages of these three methods are discussed. E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. III. Estimation of the Proximate Constituents. WALDEMAR KOCH and EMMA P. CARR (*J. Amer. Chem. Soc.*, 1909, 31, 1341—1355. Compare preceding abstracts).—Methods are described for effecting the separation and estimation of the six classes of constituents referred to by Koch, and the results of the analysis of a sample of meat by these methods are tabulated. E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. IV. Estimation of the Elements, with Special Reference to Sulphur. WALDEMAR KOCH and FRED. W. UPSON (*J. Amer. Chem. Soc.*, 1909, 31, 1355—1364. Compare preceding abstracts).—Methods are described for estimating the total sulphur in animal tissues and its distribution in the lipoids, extractives, proteins, and inorganic sulphates. In the lipoids, extractives, and proteins, the sulphur exists in both the oxidised and non-oxidised condition, the former being represented by the ethereal or $R \cdot SO_2 \cdot OH$ type, and the

latter by the cystine or R·S·H type. Methods are given for the estimation of the sulphur in each of these states of combination.

The results of a study by these methods of the distribution of sulphur in brains of three different ages are tabulated. The percentage of total sulphur does not show any great variation. The results indicate, however, that the lipoid sulphur increases at first with age and decreases later, and the organic sulphur compounds, soluble in water, decrease with age. E. G.

Volumetric Estimation of Phenol by Lloyd's Method. Tribromophenol Bromide and Hexabromophenoquinone. S. C. J. OLIVIER (*Rec. trav. chim.*, 1909, **28**, 354—367).—In the author's experience, Koppeschaar's process for the estimation of phenol does not, as Lloyd states (Abstr., 1905, ii, 209), give inaccurate results, and on the contrary the modified form described by Lloyd (*loc. cit.*) gives results less trustworthy than those given by the original process. In this investigation, the author prepared tribromophenol bromide and hexabromophenoquinone, and records certain new data regarding these substances.

Tribromophenol bromide, when heated in an atmosphere of carbon dioxide, begins to evolve bromine even below 100°, and it is to this decomposition that the different melting points ascribed to this substance are due. Mixed with excess of potassium iodide and hydrochloric acid, the bromide liberates 99·6% of the theoretical quantity of iodine, so that the anomalous results recorded by Lloyd cannot be due, as he suggests, to the formation of this substance in the titration of phenol by Koppeschaar's process.

Hexabromophenoquinone was prepared by Benedikt's process (Abstr., 1879, 717), but could not be obtained crystalline. This substance is not formed when excess of bromine is allowed to react with phenol under the conditions prescribed by Koppeschaar, so that Lloyd's anomalous results with this process are not due to this cause.

In using Koppeschaar's process, the time of action of the bromine on the phenol may be reduced to five minutes if not more than 0·09 gram of phenol is used, and if the solution of sodium bromide and bromine is about 0·8 decinormal. The addition of sodium bromide inhibits the formation of tribromophenol bromide. The end reading is clearer if chloroform is added, as suggested by Lloyd (*loc. cit.*). T. A. H.

Application of Arsenious Acid in Volumetric Analysis. I. FRANZ M. LITTERSCHEID and J. BORNEMANN (*Zeitsch. angew. Chem.*, 1909, **22**, 2423—2427).—*Estimation of Dextrose* [*in Urine*].—Fifty c.c. of copper sulphate solution (49·948 grams per litre) are placed in a 200 c.c. measuring flask, 20 c.c. of the usual alkaline tartrate solution are added, and the liquid is heated to boiling. Twenty-five c.c. of the dextrose solution (urine), not exceeding 1% in strength, are added, and the boiling is continued for two minutes. To the hot liquid are then added 50 c.c. of arsenious acid solution (9·9 grams per litre; this is equivalent to the copper solution), and also 30 c.c. of 96% acetic acid. When cold, 7 grams of potassium iodide are added in six to eight

portions. When all the copper, including the reduced oxide, has passed into cuprous iodide, the liquid is diluted to the mark and filtered, the first portion of 10 c.c. being rejected. One hundred c.c. are then nearly neutralised with 20% sodium hydroxide, and, after adding 5 grams of sodium hydrogen carbonate and diluting to 400—500 c.c., the free arsenious acid is titrated with *N*/10-iodine as usual. Or the liquid may be nearly neutralised with pure ammonia and diluted to 400—500 c.c. without addition of hydrogen carbonate. The arsenious acid found is equivalent to the copper reduced by the dextrose. A table is given showing the amount of dextrose corresponding with the c.c. of iodine used. L. DE K.

Simple Distilling Apparatus for the Estimation of Pentosans by Tollens' Method. JOHANN TISCHTSCHENKO (*J. Landw.*, 1909, **57**, 229—230).—The usual apparatus consists of a flask fitted with a tap funnel and a Kjeldahl distilling bulb, to which the condenser is attached. This is now simplified by making the funnel and bulb in one piece, the funnel passing down through the middle of the bulb; the double boring of the cock is thus avoided. A sketch is given.

N. H. J. M.

[Estimation of Glycogen.] KARL GRUBE (*Pflüger's Archiv*, 1909, **130**, 322—324). EDUARD PFLÜGER (*ibid.*, 325—327).—Polemical.

Quantitative Estimation of Lactic Acid in Cheese. SHIGEHIRO SUZUKII and EDWIN B. HART (*J. Amer. Chem. Soc.*, 1909, **31**, 1364—1367).—In connexion with a study of the chemical changes which take place during the ripening of cheese, it was necessary to find a trustworthy method for estimating lactic acid. Palm's method (Abstr., 1887, 307), depending on the formation of basic lead lactate, $3PbO,2C_3H_6O_3$, has been found to be inaccurate. Partheil's method (Abstr., 1903, ii, 189), in which the lactic acid is distilled in a current of superheated steam, when applied to *i*-lactic acid, must not be carried out below 130°, and the distillation must be continued until 750 c.c. of distillate have been collected. This method, however, cannot be used in presence of other acids, such as malic, citric, tartaric, oxalic, or succinic, and is therefore unsuitable for cheese analysis. The usual method of estimating lactic acid by adding dilute sulphuric acid to the cheese, extracting with ether, and afterwards separating the acid in the form of its zinc salt, gives fairly satisfactory results when carefully carried out. E. G.

Estimation of Cinnamic and Benzoic Acids in Mixtures of the Two Acids. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1909, **28**, 342—348. Compare Abstr., 1908, ii, 993).—The methods already described, such as those of de Jong (Abstr., 1906, ii, 315) and Scheringa (Abstr., 1907, ii, 823), give good results for the volumetric estimation of these two acids, but are unsuitable in cases where other acids are present, or where the constituents must also be isolated and identified.

In the process now described, cinnamic acid is converted into

dibromophenylpropionic acid, which can be separated quantitatively from benzoic acid and identified.

Preliminary experiments with mixtures of the two acids by (1) fractional crystallisation; (2) extraction by solvents; (3) sublimation, and (4) precipitation of metallic salts, did not give promising results.

The process eventually discovered consists in dissolving the mixture under examination in carbon disulphide and determining, either by titration or weighing, the bromine necessary to convert the cinnamic acid present into dibromophenylpropionic acid. This may then be separated quantitatively from benzoic acid by extracting the latter with carbon tetrachloride or by removing it by sublimation.

T. A. H.

Sodium Phosphotungstate as a Reagent for Uric Acid and other Reducing Substances. CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1909, **61**, 434—437).—The reaction in urine with sodium phosphotungstate described by Richaud and Bidot depends on the presence of uric acid, which reduces the reagent and forms a blue colour. Other reducing substances (dextrose, hydroxylamine, morphine, etc.) give the same reaction. The blue colour which ferrous salts give with the tungstate passes in the presence of atmospheric oxygen into a green and then a red colour, as lower tungsten oxides are formed. Reducing agents produce analogous changes in molybdic salts.

W. D. H.

The Iodine Reaction of Adrenaline. LUDWIG KRAUSS (*Biochem. Zeitsch.*, 1909, **22**, 131).—A question of priority. The author claims that the reaction with iodic acid described by Fränkel and Allers (Abstr., 1909, ii, 628) was previously described by himself (*Apoth. Zeit.*, 1908, 701).

W. D. H.

Estimation of Morphine in Opium; Extract of Opium and Tincture of Opium. HEINRICH FRERICHS (*Chem. Zentr.*, 1909, ii, 1499—1500; from *Apoth. Zeit.*, 1909, **24**, 592—596).—Helfenberger's process is recommended, using 5 grams of dilute ammonia (17 + 83) and water saturated with ether. A convenient separating funnel for washing the morphine crystals is described. The process is also applicable to the extract and the tincture of opium; the latter should be concentrated to about one-third. Opium may be reduced to a definite morphine content by addition of starch; for the extract, lactose may be used.

L. DE K.

Estimation of Urea in Urine. P. W. GILL, F. G. ALLISON, and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, **31**, 1078—1093).—A modification of the hydrolysis method. The resulting solution, after heating the urine with hydrochloric acid in an autoclave, is mixed with an excess of sodium carbonate, and the ammonia formed from the urea is then expelled in a current of air and absorbed in standard acid. Under these conditions, no ammonia is yielded by the products of the hydrolysis of creatinine, uric acid, or hippuric acid. A special aeration apparatus is described.

L. DE K.

Estimation of Urea, Allantoin, and Amino-acids in Urine. DOROTHY E. LINDSAY (*Bio-Chem. J.*, 1909, **4**, 448—454).—Nitrogen is estimated by (*a*) Bohland's method; this gives the nitrogen of amino-acids, hippuric acid, creatinine, allantoin, and urea. Estimation by Folin's method (*b*) gives the nitrogen of urea, allantoin, and ammonia; estimation by the Mörner-Folin method (*c*) gives the nitrogen of urea and ammonia. Ammonia and creatinine are estimated separately by Folin's method. The difference between (*a*) and (*b*) gives the nitrogen of amino-acids (including hippuric acid) and of creatinine; the difference between (*b*) and (*c*) gives the allantoin nitrogen. This combination of methods was found to give good results with artificial mixtures.

W. D. H.

Estimation of Purine Bases in Urine. ERNEST L. KENNAWAY (*J. Physiol.*, 1909, **39**, 296—310).—When urine is treated by the Camerer-Arnstein method for the estimation of total purines, uric acid loses ammonia; this loss occurs when the precipitate of silver-magnesium urate is boiled. The purine bases do not undergo this loss. The method is, therefore, only correct when employed for the estimation of purine bases in urine from which the uric acid has been removed.

W. D. H.

Vanillin as a Test for Antipyrine and Kryogenine; Detection of Antipyrine in Pyramidone. CHARLES PRIMOT (*Chem Zentr.*, 1909, ii, 479; from *Bull. Sci. Pharmacol.*, 1909, **16**, 270).—If a small crystal of antipyrine is moistened with 2 c.c. of a reagent consisting of 1 gram of vanillin, 6 grams of dilute hydrochloric acid (1 : 1), and 100 grams of 95% alcohol, and the whole evaporated on the water-bath, a dark orange-yellow ring is formed first, and afterwards a similar stain on the bottom of the dish is noticed. The test shows the presence of even 0·00095 mg. of antipyrine. Pyramidone does not give the test, and even 0·005 mg. of antipyrine may thus be detected in 0·1 gram of pyramidone. Kryogenine gives a distinct greenish-yellow coloration when this test is applied.

L. DE K.

Attempt to Estimate Indoxyl in Urine. L. A. MENNECHET (*Chem. Zentr.*, 1909, ii, 1499; from *Bull. Sci. Pharmacol.*, 1909, **16**, 458—460).—The urine is defecated by 10 vol. % of basic lead acetate, and a portion of the filtrate, representing 50 c.c. of the urine, is mixed with an equal volume of pure hydrochloric acid. After shaking for five minutes, 5 c.c. of chloroform are added, and the shaking is continued; if the chloroform remains colourless, 2 to 3 drops of hydrogen peroxide solution are added. The chloroform is drawn off, and the liquid is shaken repeatedly with fresh portions of chloroform. The united chloroform extracts are shaken, first with water containing a few drops of sodium hydroxide and then with water, and the indoxyl is titrated by means of standard hypobromite. The chloroform does not become quite colourless at the end of the titration, but retains a slight lilac colour.

L. DE K.

Cause of the Vanillin Hydrochloric Acid Reaction for Camphor. O. TUNMANN (*Chem. Zentr.*, 1909, ii, 1010; from *Schweiz. Wochschr. Chem. Pharm.*, 1909, 47, 517—519).—The active substance contained in commercial camphor, to which the reaction with vanillin and hydrochloric acid is due, is only an impurity, and is not derived from the oil cells of the camphor tree, but exists in the parenchyma cells. It is probably closely related to the phloroglucotannoids, and it seems to play an important physiological rôle. L. DE K.

A Colour Reaction for Gelatin. R. ED. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 248).—Mixed aqueous solutions of cupric chloride and excess of tripotassium phosphate give, in the presence of gelatin, a violet coloration instead of the usual whitish-green precipitate. G. S. W.

The Value of Benzidine for the Detection of Minute Traces of Blood. E. J. MCWEENEY (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 12, 216—223).—The reagent is made by dissolving a pinch of benzidine in 3—4 c.c. of glacial acetic acid just before use, for the mixture itself turns blue after about a minute, 0·5 c.c. is transferred to a test-tube, and 2 c.c. of 10% hydrogen peroxide are added. To the white, opaque mixture is added the material to be examined for blood, and its presence is denoted by an immediate blue coloration. The material requiring investigation consists nearly always of suspected stains, and may be usually obtained as a fine dust by scraping. Should it be found impracticable to obtain a scraping, the fabric may be treated with a drop of normal saline solution, the stained fibres removed to another slide, and treated between slide and cover-glass with a drop of the reagent, when the presence of blood reveals itself by the brilliant blue coloration of the affected fibre. The mass may then be treated on the slide with a drop of 32% potassium hydroxide, so as to render visible the outlines of the individual red cells.

None of the secretions and excretions hitherto tested by the author (saliva, nasal mucus, urine, etc.) has been found to behave towards benzidine in the same way as blood, but precisely similar results are given by many freshly-cut vegetables and fruits (potato and apple for instance), but these no longer give the reaction when boiled for some time, whereas the reaction given by blood solutions is unimpaired by boiling for ten minutes.

A positive result with the benzidine test should not be looked on as absolutely positive proof of the presence of blood, although if the result is negative the absence of blood may be safely assumed. No regard should be paid to colour changes occurring after the lapse of one minute, and a blank test should be made to make sure that the materials and the test-tubes to be used are satisfactory. L. DE K.

General and Physical Chemistry.

Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen and their Relations. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, **83**, *A*, 151—171).—On account of the discrepancies exhibited by existing data, the authors have redetermined the refractivities of the four gases for the wave-lengths $\lambda = 6563$, 5790, 5461, and 4861. In all cases it is found that Cauchy's formula, $\mu - 1 = a(1 + b/\lambda^2)$, is inadequate for the expression of the dispersion data, the value of b increasing as the wave-length diminishes. Much better agreement is obtained when a formula of the Sellmeier type is employed to represent the results. The constants involved in the Sellmeier formula are calculated for each of the four gases examined, and also for phosphorus, sulphur, and mercury.

H. M. D.

Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide and their Relation to those of their Constituents. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, **83**, *A*, 171—176).—Measurements of the dispersion of sulphur dioxide and hydrogen sulphide are recorded, and the data are expressed in terms of Sellmeier's formula, for which the constants involved are calculated.

The refraction data for sulphur dioxide and hydrogen sulphide are compared with those of the component elements, and it is shown that the refractivity does not follow an additive law. For sulphur dioxide the refractivity is 18%, and for hydrogen sulphide 6%, less than that required by the law of addition. Whereas the number of dispersion electrons in sulphur dioxide appears to be equal to the sum of the dispersion electrons in sulphur and oxygen, this relationship does not hold in the case of hydrogen sulphide. H. M. D.

Refraction and Dispersion of Neon. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, **83**, *A*, 149—151).—The refractive index of neon at 0° and 760 mm. was found to be 1·00006716 for the green mercury line ($\lambda = 5461$). From this and values obtained for the red and blue lines of cadmium, the dispersion has been calculated. Previous measurements having shown that the refractivities of the inert gases are very nearly in the ratio of whole numbers, it was anticipated that the refractivity of neon would be exactly twice as large as that of helium. The experimental value is, however, less than this to the extent of 4%.

H. M. D.

Distribution of the Ultimate Rays in the Spectrum of Different Regions of the Sun. ANTOINE DE GRAMONT (*Compt. rend.*, 1910, **150**, 37—40. Compare Abstr., 1908, ii, 645).—This paper contains a tabular statement of the wave-lengths for the

ultimate rays of great persistency found in the sun. The fact that metalloids, such as tellurium, phosphorus, arsenic, antimony, and boron, have never been recognised in the sun is probably to be explained by the absorption of their ultimate rays by the terrestrial atmosphere.

The author considers that Lockyer's enhanced lines are not due to dissociation, but that they are ultimate rays, and that their appearance gives some indication as to the proportions in which the elements producing them are present. W. O. W.

Critical Study of Spectral Series. I. The Alkalis, Hydrogen and Helium. William M. Hicks (*Proc. Roy. Soc.*, 1910, **83**, *A*, 226—228*).—The experimental measurements of the spectral lines of the alkali metals, hydrogen and helium, have been analysed with the object of determining the relationships between the wave-length numbers. For any one series of lines, the wave numbers can practically all be represented by a modified Rydberg formula. The relationships between certain constants for the series (lithium, sodium, potassium, rubidium, cæsium) are expressible by the integers 1, 2, 4, 5, and 6, and these integers are also involved when the atomic volumes of the respective alkali metals are compared. H. M. D.

Line Spectrum of Calcium given by the Oxy-acetylene Burner. Gustave A. Hemsalech and Charles de Watteville (*Compt. rend.*, 1909, **149**, 1112—1115).—Using the method described previously (Abstr., 1908, ii, 336, 445, 547, 745), the authors have investigated the spectrum of calcium in the oxy-acetylene flame. The flame contains a very brilliant blue cone, which shows not only the bands which are obtained with a Bunsen burner, but also a series of supplementary bands which are distributed over the whole length of the spectrum. A full list of wave-lengths and intensities is given.

All the calcium lines do not exist at the base of the flame, but are only formed some distance above the orifice of the burner. Even the strongest lines, although visible, are only very faint at the base of the flame; they become very intense just above the blue cone.

A table is given showing that with flames of different temperatures the number of lines between λ 3900 and λ 5000 increases with increasing temperature. It is also shown that the number of lines given by that portion of the flame which extends to the top of the blue cone decreases with rise in temperature. T. S. P.

The Yellow, Orange, and Red Regions of the High Temperature Flame Spectrum of Calcium. Gustave A. Hemsalech and Charles de Watteville (*Compt. rend.*, 1909, **149**, 1369—1372).—The authors compare the less refrangible part of the calcium spectrum obtained by them in the oxy-acetylene flame (preceding abstract) with the spectrum obtained by King (*Astrophys. Journ.*, **29**, 190) with the electric furnace. With the exception of the line $\lambda = 6708{\cdot}18$, which is present in the latter spectrum and not in the former, the characters of the spectra are the same, and the causes which produce them are therefore probably thermal. In order to produce the red lines in the

* and *Phil. Trans.*, 1910, *A*, **210**, 57—111.

calcium spectrum, a high temperature, such as that given with the oxy-acetylene flame, is necessary.

The line $\lambda = 6708 \cdot 18$, which is present in the spectrum of the electric furnace, is probably due to lithium ($\lambda = 6708 \cdot 08$). This same line is found in the sun-spot spectrum, and therefore lithium is present in the sun. T. S. P.

Series Systems in the Spectra of Zinc, Cadmium, and Mercury. T. ROYDS (*Ann. Physik*, 1909, [iv], **30**, 1024).—In reference to Paschen's paper (this vol., ii, 3), the author points out that he has already measured the Zeeman effect for certain lines in the spectra of zinc and cadmium. In a magnetic field, the lines 6438·7 (cadmium), 6362·6 (zinc), 5528·7 and 4703·3 (magnesium) appear as symmetrical triplets. The magnetic displacement observed for these lines corresponds with values of e/m in good agreement with the value for cathode rays. H. M. D.

The Spectrum of Antimony. A KRETZER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1910, **8**, 45—72).—The spark, arc, and flame spectra of antimony have been investigated. The wave-length measurements of the lines and bands are recorded in detail, and compared with the data of previous observers. H. M. D.

Absorption Spectrum of Potassium Vapour. P. V. BEVAN (*Phil. Mag.*, 1910, [vi], **19**, 195—200).—It has been found that the principal series lines of potassium appear in much greater numbers in the absorption spectrum of potassium vapour than in any form of emission spectrum which has as yet been examined. This result is analogous to that obtained by Wood in the case of sodium vapour.

The method of experiment consisted in heating potassium in a steel tube, the ends of which were closed by quartz plates. A beam of light was passed through the tube, and the emergent beam was examined by means of a quartz spectrograph. In this way the author was able to measure the wave-lengths of the principal lines of potassium up to the line corresponding with $n = 26$ in the Kayser and Runge formula. Hitherto the members of the series up to $n = 11$ have been observed, so that fifteen new lines have been added to the list. The wave-lengths of these range from 2928·0 to 2870·0.

A comparison of the absorption spectra of sodium and potassium vapours shows a close correspondence between them, and this is regarded as evidence that the mechanism involved in the two cases is the same. H. M. D.

Absorption Spectra of Various Salts in Solution, and the Effect of Temperature on Such Spectra. XXVI. HARRY C. JONES and W. W. STRONG (*Amer. Chem. J.*, 1910, **43**, 37—90).—A detailed account is given of an investigation of the absorption spectra of various potassium, uranium, and neodymium compounds by the methods employed by Jones and Uhler (Abstr., 1907, ii, 147, 211, 212) and by Jones and Anderson (Abstr., 1909, ii, 197, 359). The absorption spectra of potassium ferricyanide, ferrocyanide, chromate,

and dichromate, and of uranyl acetate, bromide, chloride, nitrate, and sulphate in aqueous solution, of uranyl acetate, nitrate, and chloride in methyl alcohol, and of uranyl nitrate and chloride in ethyl alcohol are recorded. The effect of dehydrating agents, such as calcium and aluminium chlorides, has been determined. Photographic records have been obtained of the absorption spectra of uranous chloride and sulphate, and the absorption spectra of neodymium chloride in glycerol and in mixtures of glycerol and water have been studied. The effect of changes of temperature of solutions of various salts at different concentrations has been investigated, and spectrograms for a given concentration of a salt have been made at 0°, 15°, 30°, 45°, 60°, 75°, and 90° for a layer of constant thickness.

The absorption spectra of the uranyl salts contain a series of bands in the blue and violet which are usually diffuse. The position of the uranyl bands is not affected by dilution. In methyl and ethyl alcohol, the bands of each particular salt occupy different positions. A new set of fine bands in the green has been discovered in the spectrum of aqueous solutions of uranyl chloride; the presence of a small quantity of aluminium or calcium chloride causes them to disappear.

The absorption spectra of the uranous salts are quite different from those of the uranyl compounds.

The absorption spectrum of neodymium chloride in glycerol differs entirely from that of an aqueous solution.

The intensity of the phosphorescence of the same uranyl salts obtained from different solvents by evaporation is found to vary greatly. Monochromatic stimulation fails to excite phosphorescent bands until the wave-lengths reach the region of the uranyl bands.

The NO_3 group has a great influence on the frequency of the uranyl and uranous absorption bands, and of the uranyl phosphorescent bands. E. G.

A Relation between Absorption and Phosphorescence. L. Brüninghaus (*Compt. rend.*, 1909, **149**, 1124—1127).—The absorption and phosphorescence spectra of the rare earths are discontinuous, consisting generally of narrow bands. In the absorption spectra, groups of absorption bands are separated by regions of transparency, whereas in the phosphorescence spectra the regions of emission are separated by dark regions. Taking the spectra of praseodymium, erbium, dysprosium, terbium, and samarium as examples, the author shows: (1) that the mean regions of emission are generally little separated from the mean regions of absorption, and (2) that the regions of emission do not coincide with the regions of absorption, but with the transparent regions (either those between the groups of absorption bands or those outside them). There is thus an alternation between the groups of absorption bands and those of phosphorescence.

The results obtained with compounds of the common elements, such as manganese, chromium, iron, copper, etc., confirm those given above. In general, these substances phosphoresce with a colour which is little different in shade from their colour by reflected or transmitted light. For example, chromium sesquioxide when dissolved in alumina gives

the ruby, which phosphoresces with a red light; when dissolved in lime it is green, and the phosphorescence is green.

It seems as if the light emanates from "phosphorogenic" molecules in the interior of the phosphorescent substance. This light undergoes absorption in the superficial layers, and the radiations observed at the surface are only those for which the "phosphorogenic" substance is relatively transparent. T. S. P.

Theory of the Law of the Optimum of Phosphorescence L. Brüninghaus (*Compt. rend.*, 1909, **149**, 1375—1377.)—Making use of the ideas put forward in a previous paper (preceding abstract), the author develops a relation connecting the intensity (I) of the radiation comprised between two wave-lengths, λ and $\lambda + d\lambda$, which are very close together, and the concentration (c) of the phosphorogenic substance in a phosphor. The relation is $I = kce^{-Bc}$, where k and B are constants, B depending on the phosphorescent substance. T. S. P.

Electrolytic Conductivity of Fluorescent Solutions. A. Rassenfosse (*Bull. Acad. roy. Belg.*, 1909, 995—1107).—According to the theory of de Heen, the conductivity of a fluorescent solution should depend on the light to which it is exposed. Experiments on solutions of fluorescein and eosin show that the conductivity is a maximum when they are submitted to the action of light which is absorbed by them, green in the case of fluorescein, and yellow in the case of eosin. Blank experiments on solutions of potassium chloride proved that the conductivity does not vary under the action of light of different colours, and also that the observed variation in the case of the fluorescent solutions is not a thermal effect. T. S. P.

Luminescence of Crystals. Alfredo Pochettino (*Nuovo Cimento*, 1909, [v], **18**, 245—300. Compare Abstr., 1905, ii, 430).—The phenomenon of luminescence has been investigated for 227 specimens of crystals representing 78 kinds of minerals. Several methods of exciting luminescence were used; the more important results were obtained with cathode luminescence, but the anodic luminescence, fluorescence, phosphorescence, and thermoluminescence of the crystals were also investigated when they occurred.

In many cases the nature of the luminescence depends upon the method of excitation, thus for distene the ordinary phosphorescence and the cathode luminescence are of different colours, and in the case of calcite the ordinary fluorescence is polarised and the cathode luminescence is not. The nature of the spectra of the cathode luminescence is in many cases independent of the *E.M.F.* applied to the vacuum tube, but the intensity of the luminescence is generally greater the greater the applied *E.M.F.*, provided the crystals undergo no permanent changes under the influence of the rays. There does not appear to be any definite connexion between the luminescence of crystals and their mineralogical relationships; even crystals of the same substance from different sources may show luminescence of different colours, and some specimens of quartz show luminescence whilst others do not.

Many observations have been made on the orientation of the plane of polarisation of the polarised part of the luminescence. The mineral milerite is dichroic, greenocite shows double cathodic luminescence, and the light emitted from the face of crystals of cassiterite parallel to the z axis is totally polarised. With one exception, the luminescence emitted from crystals of the rhombohedric system is not rectilineally polarised. The greater the exhaustion of the vacuum tube the more completely is the luminescence polarised, and, in general, all causes which tend to diminish the total intensity of the light emitted diminish the degree of polarisation of the light.

The effect of cathode rays on the minerals is discussed. Many minerals become brown under these conditions, and on the face of a crystal directly exposed to the rays a stain made up of differently coloured concentric rings is sometimes observed. On continued exposure to cathode rays, the capacity of a crystal to become luminous by excitation of the rays diminishes, and this diminution may be temporary or permanent. Fewer substances are rendered luminous by anode rays than by cathode rays, and every mineral so far examined which shows anodic luminescence can also be rendered luminous in some other way. In all cases the luminescence due to anode rays is weakest, less durable, and less polarised than that produced by cathode radiation under corresponding conditions.

G. S.

Dependence of the Photo-electric Effect of the Alkali Metals in Polarised Light on the Wave-length. ROBERT POHL (*Ber. Deut. physikal. Ges.*, 1909, 715—722).—Experiments with an alloy of potassium and sodium and ultra-violet radiation of short wave-length show that the photo-electric behaviour of the alkali metals in polarised light is the same as that observed in the case of other metals.

H. M. D.

Theory of the Ripening Process of the Silver Haloids. A. P. H. TRIVELLI (*Zeitsch. wiss. Photochem.*, 1910, 8, 17—24).—As the result of a microscopic examination of ripened silver haloid plates of high sensitiveness, the author concludes that the ripening process is due to the development of definitely recognisable crystalline structure. In consequence of this structural change, the silver haloid is in a condition of strain, and in consequence is less stable than in the unripened condition. The smaller degree of stability is supposed to be the cause of the greater photo-sensitiveness.

H. M. D.

New Determinations of the Radioactivity of the Thermal Waters of Plombières. ANDRÉ BROCHET (*Compt. rend.*, 1910, **150**, 145—148).—The author has redetermined the radioactivity of the waters of Plombières (compare Abstr., 1908, ii, 143). The radioactivity of the gases spontaneously liberated from the various waters was measured, and then the latter were agitated with an equal volume of air, and the radioactivity of the latter measured in the apparatus of Chéneveau-Laborde. The tabulated results give the

altitude of the spring, the outflow per twenty-four hours, mean temperatures in 1859—1861, Sept., 1908, and August, 1909, the total solids per litre, the radioactivities in milligram-minutes per 10 litres of the gases and the waters, and the total radioactivity for twenty-four hours.

The waters are strongly radioactive, the radioactivity being due to radium emanation. The total radioactivity of the 22 springs is 74620 milligram-minutes for an average outflow of 67244 cubic metres of water per twenty-four hours. The average radioactivity is 1·11 milligram-minutes per 10 litres, the Lambinet water being the most active (2·18). It is calculated that 55—60 mgms. of radium bromide are contained in the total output of water per minute (507 litres). This quantity is defined as the *radioactive power* of the Plombières waters. T. S. P.

The Recoil of Radium-*C* from Radium-*B*. WALTER MAKOWER and SIDNEY RUSS (*Phil. Mag.*, 1910, [vi], **19**, 100—115. Compare Abstr., 1909, ii, 455).—The active deposit of radium on a platinum plate was mounted opposite a metal disc in an exhausted tube for some minutes, so that the disintegration products recoiling from the plate would be received on the disc. The plate was first freed from adhering emanation and from radium-*A* by heating at 360° in a vacuum for half an hour before use. It was found that, in general, both radium-*B* and -*C* were radiated to the disc, but if three hours elapsed between the preparation of the active deposit and the recoil experiment, only radium-*C* was obtained. They consider that the radiation of radium-*C* may not in all cases be a primary recoil effect, but due to mechanical disturbance produced by the recoil of radium-*D*. The amount of radium-*C* recoiled varies with the same plate with the time in an unexplained manner, and is always small compared with the amount of radium-*B* recoiled. Since radium-*B* gives only a β-particle, it is to be expected that radium-*C* will recoil with far less energy than radium-*B*, which results from the recoil of the α-ray-expelling radium-*A*. But the energy of the recoiling radium-*B* atom is apparently far greater than theory would indicate. Its power of penetrating air is about 1/40th of that of recoiling radium-*B*. Attempts to detect an electric charge on the recoiling radium-*C* atom have failed (compare Makower, Abstr., 1909, ii, 456; *Le Radium*, 1909, **6**, 50). F. S.

Disengagement of Emanation from Radium Salts. L. KOLOWRAT (*Le Radium*, 1909, **6**, 321. Compare Abstr., 1907, ii, 729).—The paper is devoted to a detailed reconsideration of many of the points previously discussed. The anomaly encountered, in that the disengagement of emanation from radiferous barium chloride decreases with rise of temperature from 830° to a minumum at 920°, and then increases again quickly to the m. p. at about 950°, is probably explained by Plato's observation of the existence of two forms of barium chloride with transformation point 34·4° below the m. p. (Abstr., 1907, ii, 239). Similar behaviour of barium fluoride indicates a similar polymorphic transformation between 1000° and 1100°.

Additional salts studied comprise potassium nitrate, silver chloride, and cæsium nitrate. Nineteen series of experiments have been made on the growth with time of the amount of emanation retained by the salts at varying temperatures, after complete initial removal of the emanation by fusion, both when the temperature is maintained and also when during part of the time the salt is not heated. The results are interpreted on the view that a definite temperature, different for different molecules, exists for each molecule of emanation formed within the salt, below which it is retained. The amount of emanation retained at any temperature is the sum of all the molecules the temperatures of disengagement of which are above that temperature. No evidence of any want of homogeneity of the emanation disengaged at different temperatures was obtained (compare Rutherford, Abstr., 1909, ii, 457; Debierne, *ibid.*, 534). F. S.

Nature of the Ionisation of a Molecule by an α-Particle. R. D. Kleeman (*Proc. Roy. Soc.*, 1910, **83**, *A*, 195—199).—If the energy of ionisation is derived from the kinetic energy of the α-particle, the electrons ejected from molecules should on the whole possess a a motion in the direction of the α-particles. In the experiment designed to test this, α-particles from a plate covered with polonium were passed through a very thin aluminium foil, and fell on a parallel aluminium plate in hydrogen and also in air at a low pressure. If the emergent electrons from the foil are more numerous than the incident electrons from the plate, when an electric field is applied between the foil and plate, the current should be larger with the foil negative than vice versa, and this difference should be the more marked as the potentials are increased. Experiments in hydrogen at 0·8 mm. pressure show a well marked difference, increasing rapidly as the voltage is increased above the point at which the expelled electrons acquire sufficient velocity to ionise by collision. The experiments support the view that the energy of ionisation is derived from the ionising agency, not by "trigger" action, from an internal store in the molecule ionised. F. S.

The Number of α-Particles Expelled from the Actinium and Thorium Emanations. H. Geiger and E. Marsden (*Physikal. Zeitsch.*, 1910, **11**, 7—11. Compare Bronson, Abstr., 1908, ii, 792).—By a further development of the method of counting α-particles by the scintillations produced in zinc sulphide, interesting confirmation and extension have been obtained of Bronson's conclusion that the thorium emanation must give at least four α-particles and the actinium emanation at least two α-particles on disintegration. The number of scintillations produced by the emanation and active deposit together in equilibrium and by the active deposit alone, after the supply of emanation has been stopped and the emanation allowed to decay, is as 3 to 1 both for thorium and actinium, showing that the emanation produces twice the number of α-particles produced by the active deposit. The thorium active deposit is known to produce two α-particles. [A similar conclusion in the case of the actinium active deposit (compare Blanquies, Abstr., 1909, ii, 634) is not referred to.]

Emanation was allowed to diffuse between two parallel zinc sulphide screens placed close together, film side inwards, and the number of scintillations on exactly opposite portions of the two screens counted simultaneously by two observers with two microscopes. For actinium emanation a very large proportion of the scintillations, up to 66%, occurred in pairs, showing that two particles are expelled simultaneously or a least with less than 0·1 second between them. With radium emanation and active deposit in equilibrium, only 2 to 4% of pairs was observed. For thorium emanation it was established that the four α-particles expelled were not simultaneous. A large number of cases of *successive* scintillations in similar parts of the field were observed, with a time interval between the two scintillations from half a second to an unmeasurably short time. This occurred even when extremely few scintillations were produced. The existence of at least one short-lived α-ray product in the thorium series, with a period of average life of about 0·2 second, is indicated, but full elucidation of this case is not yet arrived at. F. S.

The Absorption of Cathode Rays of Different Velocity in Helium. JAMES ROBINSON (*Physikal. Zeitsch.*, 1910, **11**, 11—13).—The cathode rays obtained by the action of ultra-violet light on a negatively charged plate were employed. The velocity of the rays was varied by varying the charge on the plate. With decreasing velocity of cathode rays the absorption by gases attains a maximum. In hydrogen the maximum is reached more suddenly and at lower velocity than in other gases. In helium, the absorption with decreasing velocity increases at first only very slowly down to far smaller velocities than for other gases. The absorption then rises with great abruptness to the maximum. Helium thus resembles hydrogen, but the peculiarities shown by the latter gas are even more marked in helium. F. S.

Contact Electrification. ALBERT GRUMBACH (*Compt. rend.*, 1909, **149**, 846—848. Compare Gouy, Abstr., 1906, ii, 652).—According to Helmholtz the contact potential of a liquid with glass is proportional to $\rho P/\eta E$, where E is the $E.M.F.$ acquired by the liquid of viscosity η and resistivity ρ in passing through a glass capillary tube under pressure P.

The author finds that in a $N/1000$-solution of potassium chloride in water E, is strictly proportional to P. The addition of 5·6% of phenol to the solution increases the viscosity η in the ratio 1 : 1·09, but does not alter the conductivity. The capillary $E.M.F.$, however, undergoes a marked reduction. In two series of experiments the addition of phenol altered the contact potential in the ratios 1 : 0·80 and 1 : 0·78 respectively. R. J. C.

Dielectric Properties of the Elements. DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1164—1171).—As usually determined, the dielectric capacity K refers to large wave-lengths, and the index of refraction, n, to very small wave-lengths, and, in order to test Maxwell's law, $n^2 = K$, it is necessary to obtain values of n and K referring to comparable conditions. The value n_∞ of n for very large

wave-lengths may be calculated by means of Cauchy's formula, $n = A + B\lambda^{-2} + C\lambda^{-4}$, where $n_\infty = A$. But this process of extrapolation gives results agreeing with the experimental values only when λ varies within narrow limits, so that the values of n_∞ thus obtained must necessarily be somewhat inaccurate, and it is found that n^2_∞ and K have identical values only in exceptional cases.

A list is given of the values of n^2_∞ and K for such elements as have been previously investigated, and in all cases the differences between the two are considerably less than those observed for complex liquids and solids. These results confirm Schmidt's view (*Ann. Physik*, 1902, [iv], **9**, 919) that, in the elements, the molecules have an especially simple structure.

The dielectric constants of the non-metals increase with the valency in any horizontal row of the periodic system and with the atomic weight in any vertical column. For helium, $n = 1{\cdot}0000375$ or $n^2 = 1{\cdot}000075$, whilst K has the value 1·000074. For the other rare gases of the atmosphere, the calculated values of K (n^2) show a continuous increase with the atomic weight. Determinations of the dielectric constants of the metals are insufficient in number to allow of any similar regularity being observed. T. H. P.

Quantitative Relations between the Dielectric Constants and other Properties of Substances. DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1385—1406).—The author has investigated the validity of various relations between the dielectric constant and other physical constants which have been suggested by various investigators. It was shown by Obach (Abstr., 1892, 158) that for the members of certain homologous series of organic compounds, proportionality exists between the dielectric constant and the latent heat of evaporation, or $\rho/K = \text{const.}$, the actual magnitude of the ratio being different for different series. The author has calculated the value of the ratio for organic compounds belonging to nine homologous series, the mean and limiting values found being as follows: (1) propionic esters, 15·20 (14·84—15·39); (2) butyric esters, 15·41 (15·04—15·78); (3) valeric esters, 15·56 (15·03—16·27); (4) ketones, 6·00 (4·95—7·1); (5) alkyl derivatives of benzene, 31·0 (29·73—33·02); (6) aliphatic acids, 39·55 (39·06—40·05); (7) nitriles, 5·65 (4·7—7·31); (8) amines, 25·47 (25·0—26·0); (9) alkyl halogen compounds, 6·61 (6·32—6·95). The values obtained by Obach were: (10) formic esters, 11·85 (11·03—12·78); (11) acetic esters, 13·72 (13·26—14·20); (12) ethyl esters of fatty acids, 13·34 (11·15—14·20); (13) monohydric alcohols and water, 7·41 (6·22—7·91), the values for *iso*propyl (6·14) and cetyl (9·1) alcohols being of doubtful accuracy. The mean of the values obtained for groups (13), (7), (4), and (9) is 6·46; for groups (10), (11), (1), (2), (3), and (12), 14·18; for group (8), 25·47; for group (5), 31, and for group (6), 39·55, these numbers, 6·46, 14·18, 25·47, 31, and 39·55, being approximately in the ratios of 1, 2, 4, 5, and 6. When all the other compounds (inorganic as well) for which the values of ρ and K are known are included, the values of the constant have the approximate proportionate magnitudes: 0·5 : 1 : 2 : 3 : 4 : 5 : 6. The chemical nature of any particular compound

seems to have no appreciable influence in determining to which group it belongs, members of one group being compounds completely different as regards their chemical characters.

The relationship between dielectric constant and chemical constitution of a dielectric given by Thwing (Abstr., 1894, ii, 374), and expressed by the equation : $K=d(a_1K_1+a_2K_2+\ldots)/M$ (where d is the density, and M the molecular weight of the compound, $a_1,a_2 \ldots$ the atoms or atomic groups of the same kind composing the molecule, and $K_1,K_2 \ldots.$ the dielectric constants of the atoms or groups), is not confirmed by the experimental numbers collected by the author.

The relation discovered by Lang (Abstr., 1896, ii, 144) for gases, namely, $(K-1)10^6/S=\text{const.}=123(116—145)$ (S being the sum of the valencies of the atoms constituting the molecule of the gas), holds only, as far as can be ascertained, at 0° and 760 mm. pressure for the six gases obeying Maxwell's law, $K=n^2$. T. H. P.

The Conductivity of Mixtures of Dilute Solutions. J. A. GARDINER (*Trans. Roy. Soc. Canada*, 1908, [iii], 2, iii, 37—52).—Burton has recently shown that a fall in the conductivity of the solution occurs when dilute hydrochloric acid is added to a colloidal solution of silver or to a dilute solution of silver nitrate. If the ordinary law of electrolysis were followed, a rise in the conductivity should occur.

The author's experiments show that as a $N/10,000$ solution of hydrogen chloride is added to water, there is, at first, very little change in the conductivity of the solution, but as the acid solution becomes more concentrated, the conductivity gradually increases. On the addition of hydrochloric acid to silver nitrate of various dilutions, a drop in the conductivity was observed. When, however, a $39{\cdot}5\times10^{-7}$ normal silver nitrate solution was reached, this effect disappeared. A similar drop in the conductivity was observed when a dilute nitric acid solution was added to a dilute silver chloride solution. The conductivity of a silver nitrate solution steadily increased with the concentration.

It is suggested that the abnormalities here recorded may be due to : (1) the absorption of hydrogen by the platinum electrodes; (2) the hydrogen ion attracting to itself the neutral silver chloride, and becoming loaded so that its mobility falls below that of the silver ion which it displaces. E. J. R.

Cadmium Chloride Concentration Cells. EUGEN VON BIRON and B. P. APHANASSIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1175—1182).—The authors have measured the *E.M.F.* of cadmium chloride concentration cells with and without transport of the cation. In the first case, silver chloride electrodes prepared by Jahn's method were used, and one of the solutions had the same concentration and the other different concentrations for the different cells. The curve connecting the log. of the number of grams of salt per 1 gram of water in the variable solution with the *E.M.F.*, calculated for 1 equivalent of salt per litre in the constant solution, exhibits a spread-out maximum for solutions containing 6—8 equivalents of salt. This maximum corresponds with solutions in which the transport

number of the cation is zero. A line drawn parallel to the axis of log. concentrations cuts the curve in two concentrations, which would give a cell having a zero *E.M.F.*, although diffusion would occur. If the concentrations of the two solutions are below the maximum point on the curve, the positive electricity is directed from the more concentrated to the more dilute solution; that is, with the diffusion current, whilst if the concentrations are greater than the maximum, the reverse is the case.

With cells without transport, the curve connecting *E.M.F.* and log. of the concentration is approximately linear for solutions containing 1—3 equivalents of cadmium chloride, but for higher concentrations it becomes more complex. The curve does not, however, show any of the peculiar bends observed by Godlewski (Abstr., 1902, ii, 445), whose observations are inaccurate, owing to irreversible processes at the electrodes of which he took no account.

The transport numbers for the anion and cation are calculated, the values for the former agreeing well with those obtained by Hittorf's method (compare Abstr., 1908, ii, 145, 250). Concentration cells with concentrated solutions hence show the same diffusion phenomena as are observed in those with dilute solutions, and Nernst's theory of diffusion of electrolytes is justified as well for concentrated as for dilute solutions (*loc. cit.*). T. H. P.

Rapid Formation of Positive Lead Accumulator Plates. GERHARD JUST, PAUL ASKENASY, and B. MITROFANOFF (*Zeitsch. Elektrochem.*, 1909, **15**, 872—892).—The effect of repeatedly charging and discharging lead plates immersed in sulphuric acid and in mixtures of sulphuric and nitric acids is investigated. In presence of nitric acid the attack on the plates is much more rapid, lead sulphate being first formed. This is subsequently oxidised to lead peroxide. With smooth plates, however, it appears to be impossible to obtain a sufficiently adherent, coating of lead peroxide; with plates built up of a large number of small lead sheets, so as to give a large surface, good results were obtained. In the solutions containing nitric acid, lead nitrate is formed at the anode, and this is converted into lead sulphate at some distance from the surface of the plate. This distance increases as the concentration of the nitric acid increases and that of the sulphuric acid diminishes. When it is sufficiently small, an adherent deposit is obtained; when it is greater a loose deposit is formed, and when it is greater still, a precipitate of lead sulphate is produced in the solution. A solution containing 30 grams of potassium nitrate and 218 grams of sulphuric acid per litre appears to give the best results. T. E.

Volatilisation of Cathodes. VI. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1909, **15**, 930—937).—In reply to the criticism of Starck and Fischer (Abstr., 1909, ii, 718), the author says that between the value of the cathode fall of potential at which volatilisation begins and the higher value at which it ceases to increase proportionally to the cathode fall, the volatilisation is quite a definite reproducible quantity; the relation of the quantity volatilised

to the atomic weight of the metal is too striking to be regarded as accidental. He inclines to regard Starck's theory of the phenomena as a distinct advance.

New experiments with gold and platinum in oxygen and with platinum in air are described. Satisfactory measurements could not be made in these gases with other metals, because they react with the gas in circumstances which cannot be controlled. The chemical reaction causes the discharge to become intermittent, which is indicated by a telephone in the circuit. In oxygen the regular volatilisation is observed between 440 and 1200 volts cathode fall for gold and between 500 and 900 volts for platinum. T. E.

Electrode for Determining the Concentration of the CO_3'' Ion and the Condition of Silver Carbonate in Solution. JAMES F. SPENCER and MARGARET LE PLA (*Zeitsch. anorg. Chem.*, 1909, **65**, 10—15).—Pure silver carbonate is best prepared by adding a dilute solution of sodium hydrogen carbonate to a concentrated solution of silver nitrate, stirring continuously. A silvered platinum wire, covered with the freshly precipitated carbonate, has a constant potential. With pure sodium carbonate solution as the electrolyte, the value $Ag.Ag_2CO_3.N/1\text{-}CO_3'' = +0{\cdot}7545$ volt is found, and the concentration of the CO_3'' ion, c', is found in any solution by the relation $\epsilon = 0{\cdot}7545 - 0{\cdot}029 \log. c'$. The solubility of silver carbonate in water at 25° is thus found to be $1{\cdot}16 \times 10^{-7}$ mol. per litre (compare Abegg and Cox, Abstr., 1904, ii, 256), and the salt is almost completely hydrolysed.

C. H. D.

Investigation of Electrolysis with the Ultramicroscope. J. J. KOSSONOGOFF (*Physikal. Zeitsch.*, 1909, **10**, 976—986).—An arrangement is described by means of which the author has applied the ultramicroscope to the examination of solutions through which an electric current is passed. When a current is started through a solution of silver nitrate or copper sulphate, a very considerable increase in the number of bright points in the field of view of the ultramicroscope is at once observed. The view is put forward that these are associated with the ionic carriers of the electric current. In support of this it is found that ultramicroscopic effects of a special kind are observed when the potential difference between the electrodes is raised to that which corresponds with the tension of decomposition. In the case of the above-mentioned solutions, the attainment of the critical potential difference is accompanied by a very special distribution of the bright points in the neighbourhood of the cathode. At a short distance from this electrode, and parallel to it, a zone can be distinguished in which the bright points are very closely crowded together. Between this special zone and the electrode itself is a region which is almost entirely free from bright points. This is supposed to correspond with the dark cathode space in gaseous discharge. The appearance of this effect at a particular voltage affords an optical method of determining decomposition tensions.

Similar effects have also been observed at the anode in other cases.

H. M. D.

Electrolytic Oxidation of Ammonium Carbonate. Fritz Fichter and Hans Kappeler (*Zeitsch. Elektrochem.*, 1909, **15**, 937—943. Compare Brochet and Boiteau, Abstr., 1909, ii, 657).—A solution of ammonium carbonate containing 3·669 gram-molecules of ammonia and 2·494 molecules of carbon dioxide per litre was electrolysed between platinum electrodes at temperatures from 20° to 60° and with anodic current densities between 0·027 and 0·731 amperes per sq. cm. Ammonium nitrate is the principal product; neither carbamide nor nitrite could be detected. The experiments were always stopped when a comparatively small quantity of the ammonium carbonate was oxidised. The gases evolved contained carbon dioxide, ammonia, oxygen, and hydrogen; nitrogen was not found. In an open vessel the yield increases with the current density and with the temperature. In a closed vessel, however, very much worse yields were obtained; this is due to the fact that in an open vessel the solution loses ammonium carbonate rapidly, and dilute solutions give better yields than more concentrated ones. The best results were finally obtained with a current density of 0·4 to 0·6 ampere per sq. cm., a temperature of 50—60°, and a solution containing about 2 mols. of ammonia per litre, the ratio CO_3/NH_3 being 0·27; in these circumstances the current efficiency is from 82% to 97%. A solution of ammonium tetraborate gives very similar results. T. E.

Electro-catalysis. D. Alexéeff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1155—1160).—By the electrolysis of ammonium sulphate with lead peroxide electrodes, nitrogen, oxygen, and nitrous oxide are evolved, but neither nitrite nor nitrate is formed in the solution. Hence the oxidation of the ammonia does not proceed further than the stage $NH(OH)_2$, the anhydride of which is nitrous oxide, hydroxylamine forming an intermediate oxidation product. The evolution of nitrogen occurs according to the equation: $NH_2{\cdot}OH + NH(OH)_2 = N_2 + 3H_2O$. That the nitrogen and nitrous oxide developed do not arise by the formation and subsequent decomposition of ammonium nitrite and nitrate is shown by experiments on the oxidation of hydroxylamine (*vide infra*).

With solutions of ammonium sulphate containing sulphuric acid, electrolysis with lead peroxide electrodes yields only nitrous oxide and oxygen, whilst if the ammonium sulphate solution contains ammonia, pure nitrogen is obtained. In the latter case, the formation of $NH_2{\cdot}OH$ predominates over that of $(NOH)_2$, the reaction $2NH_2{\cdot}OH + (NOH)_2 \longrightarrow 2N_2 + 4H_2O$ occurring in preference to

$$(NOH)_2 \longrightarrow N_2O + H_2O.$$

The reaction between lead peroxide and hydroxylamine proceeds according to one or the other of the two equations: $2NH_2{\cdot}OH + PbO_2 = PbO + N_2 + 3H_2O$ and $2NH_2{\cdot}OH + 2PbO_2 = 2PbO + N_2O + 3H_2O$, according to whether the hydroxylamine or the peroxide is in excess. In practice, as is shown by a study of the products obtained when the reaction takes place in absence of air, a mixture of the two gases is always obtained; the amounts actually formed in two cases were: (1) 22% N_2O and 78% N_2, and (2) 30% N_2O and 70% N_2.

Thus, lead peroxide is a typical catalyst, with the peculiarity that

one-half of its action is a chemical and the other a physical process. The formation of nitrogen and nitrous oxide at lead peroxide electrodes is hence a typical electro-catalytic process. T. H. P

Manganese, Aluminium, and Copper. FRIEDRICH HEUSLER and FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1909, **65**, 110—112. Compare Ross and Gray, Abstr., 1909, ii, 859).—The fact that certain manganese-aluminium bronzes, heated above 200° and slowly cooled, become strongly magnetic, but have considerable hysteresis, has been observed previously by Heusler and by Asteroth. C. H. D.

Magnetic Dichroism of Siderite in Liquids. GEORGES MESLIN (*Compt. rend.*, 1909, **149**, 855—857. Compare Abstr., 1909, ii, 529). —Siderite, suspended in carbon disulphide or aniline, exhibits magnetic dichroism to such a high degree that the phenomena can be seen with an ordinary permanent magnet or the residual magnetism of an electromagnet. The suspensions are also slightly dichroic spontaneously.

A method of demonstrating dichroism by the optical lantern is described. R. J. C.

Magnetism of Solutions. PAUL DRAPIER (*J. Chim. Phys.*, 1909, **7**, 385—404. Compare Pascal, Abstr., 1908, ii, 927).—The author has examined the behaviour of a number of solutions when placed in a flat, vertical cell between the pointed poles of a powerful electromagnet. If the liquid has paramagnetic properties, it tends to move radially in a plane perpendicular to the lines of force, and thus forms a tumulus or convexity at the surface. This convexity is much accentuated in aqueous solutions when the surface-tension is lowered by adding a layer of ether or benzene.

An aqueous solution of ferric alum or ferric chloride shows a convexity even when only 1% of ferric salt is present, but a solution of the same concentration in ether is unaffected.

Ferric ammonium oxalate is but slightly affected, and colloidal ferric hydroxide, potassium ferrocyanide, and potassium ferricyanide are unaffected.

If a solution of ferric chloride in ether is floated on water, a striated layer is produced, which, in the field, bends downwards into the water, the striæ being displaced horizontally. Displacements are also observable if precipitated ferric hydroxide or air bubbles are suspended in the paramagnetic fluid.

Dilute manganese sulphate gives a marked convexity, but potassium permanganate none. When ether is poured on the latter solution an intermediate layer is formed, containing ether, water, manganese sulphate, and precipitated manganese dioxide, which is extremely sensitive to the magnetic field, owing to manganese sulphate and, perhaps, to free oxygen occluded in the precipitate.

Cobalt and nickel hydroxides precipitated by ammonia are also very sensitive to the magnetic field.

Chromium sulphate, cobaltous chloride, and nickel nitrate are

paramagnetic; potassium dichromate, potassium cobalticyanide, titanium sulphate, and platinum chloride are not.

The author's observations confirm the conclusion arrived at by Pascal by a different method, that as a magnetic metal becomes more and more removed from its normal (ionised) state, it loses its paramagnetism.

The magnetic capillary rise of solutions of ferric alum and ferric chloride of 5, $7\frac{1}{2}$, and 10% strengths was investigated. On increasing and decreasing the exciting currents between 0 and 10 amperes, marked hysteresis was found in the capillary rise, apart from the usual hysteresis of the magnet. This effect is supposed by the author to be true liquid hysteresis. R. J. C.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. II. and III. PAUL PASCAL (*Bull. Soc. chim.*, 1909, [iv], 5, 1110—1118; 1910, 7, 17—28. Compare Abstr., 1909, ii, 487, 788, 859).—Part of this work has been published already. From comparisons of the magnetic susceptibility of oxygen in a series of oxygenated carbon compounds, the conclusion is drawn that the value is -48×10^{-7} where oxygen is joined to two different carbon atoms, -35×10^{-7} where it is doubly linked to a carbon atom, the latter being itself joined to two oxygen atoms (as in carboxylic acids), and $+18 \times 10^{-7}$ where a single oxygen atom is doubly linked to carbon (as in aldehydes and ketones). A comparative list of (1) experimental, molecular, magnetic susceptibilities, and of (2) values calculated from the data given above, shows close concordance. The application of these rules to the case of paraldehyde lends support to the Kekulé formula for this substance.

Apart from the above effect due to the method of linking of oxygen, the value of the magnetic susceptibility of the latter is also influenced by the general structure of the rest of the molecule, and especially by the presence of (1) tertiary or quaternary carbon atoms, (2) double linkings. The first of these effects is marked when the disturbing atom is in position α or γ, and more so in positions δ and ϵ, but is very small in β, ζ, or η, and ceases beyond position θ. The presence of a double linkage shows itself in an analogous manner, and a table of corrections for the effect of double linkings in several positions is given.

The second group of conclusions lends support to Bayer's strain hypothesis, provided the carbon chain is regarded as having a roughly spiral form.

The influence of the hexamethylene nucleus on the magnetic susceptibility is estimated at $+31 \times 10^{-7}$, and with this correction the calculated value for cineol, according to Brühl and Wallach's formula, agrees with that determined experimentally.

Sulphur has the value -156×10^{-7}, and retains this in most of its organic derivatives, but in thioacetic acid the atomic susceptibility of the oxygen atom is -15×10^{-7}, as against -35×10^{-7} for the same oxygen atom in acetic acid, the greater effect in the former case being due to the presence of the sulphur atom.

The normal value for nitrogen is -58×10^{-7}, but in a cyanogen group,

or where nitrogen is directly attached to a benzene nucleus, the value becomes -48×10^{-7}. In closed chains containing carbon and nitrogen, the latter has the same value as in aromatic amines, and for purposes of calculation, the value for one CH_2 (or CH) group is replaced by that for NH (or N), with the usual total correction for the influence of the nucleus. This rule is not applicable in the case of pyridine.

T. A. H.

Thermometers as Thermo-regulators. ERHARD GLASER (*Biochem. Zeitsch.*, 1909, **23**, 5—9).—Into the thermometer which is used as thermo-regulator, platinum wires are fused at certain definite points corresponding with temperatures the constancy of which it is desired to maintain. The lowest platinum wire is always in contact with the mercury when the thermometer is immersed in the apparatus, the temperature of which is to be regulated. By means of this and another platinum wire, corresponding with the temperature which is to be maintained in the thermostat, an electric circuit is made with a coil, in which is immersed a Hahn regulator. As soon as the mercury reaches the higher point and the circuit is closed, an iron core in the Hahn regulator is drawn down by the current and shuts off the supply of gas to the burner heating the thermostat. As the latter cools, the gas is automatically lighted again by means of a by-pass. The apparatus is figured in the paper. S. B. S.

Krafft's Boiling-point Estimations and his Theory of Volatilisation. C. VON RECHENBERG (*J. pr. Chem.*, 1909, [ii], **80**, 547—555. Compare Abstr., 1909, ii, 544).—Largely polemical in reply to Krafft (Abstr., 1909, ii, 969, and Hausen, *ibid.*, 969). It is pointed out that the expression used by Krafft, b. p./0 mm., is a contradiction, as if sufficient vapour is present for the temperature to be determined there must be a vapour pressure. The effects which are attributed by Krafft to the influence of gravity are regarded by the author as due to the condensation of vapour by external cooling.

J. J. S.

Preparation of a Mixture of Constant Boiling-point and Maximum Vapour Pressure by Distillation. D. D. GADASKIN and A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1160—1163).—The authors describe experiments on the distillation of various aqueous solutions of the ether of methylene glycol under ordinary and reduced pressure (compare Abstr., 1908, i, 753; 1909, ii, 215). The results obtained are discussed by Ma ovetzki (see following extract). T. H. P.

Determination of the Composition of Constant Boiling-point Mixtures having Maximum Vapour Pressures and their Quantitative Separation by Distillation. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1171—1175. Compare preceding abstract).—The author adduces further evidence in support of his view that a binary liquid mixture, for which a maximum or minimum vapour pressure exists, may be regarded as consisting of two components, one

being the mixture of maximal or minimal vapour pressure, and the other the component present in excess. By means of aqueous solutions of the ether of ethylene glycol, it is shown that the mixture of maximum vapour pressure can be separated quantitatively by one distillation in a suitable fractionating apparatus. The quantity and composition of the mixture with maximum vapour pressure are not altered by the addition to the solution of a non-volatile substance which effects the separation of the liquid into layers, but does not give a solid phase.

T. H. P.

An Electrical Apparatus for the Direct Determination of the Water Value of a Calorimeter. W. Świętosławski (*Bull. Acad. Sci. Cracow*, 1909, 548—555).—The principle of the method consists in using two calorimeters, which are heated by means of an electric current. The one calorimeter (chief calorimeter) is filled with the solution the water value of which is required, and the other (water calorimeter) with water. The heating is accomplished by means of a platinum wire spiral, which is fused in between two concentric layers of glass. The two vessels are of the same construction. The heat coefficient a is calculated from the formula:

$$a = \Delta T_1(500 + c_1 + c_1')/\Delta T_2(500 + c_2 + c_2'),$$

where ΔT_1 and ΔT_2 denote the increases in temperature, c_1 and c_2 the water values of the calorimeter with stirrer and thermometer, c_1' and c_2' the water values of the heating apparatus, and where each calorimeter contains 500 grams of water.

The sp. heat K of any liquid can then be calculated from the equation $K = a\Delta T_2/\Delta T_1$, where the increases in temperature of the two calorimeters are ΔT_1 and ΔT_2.

J. J. S.

Atomic Volume of Allotropic Modifications at Very Low Temperatures. Ernst Cohen and J. Olie, jun.* (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 437—445).—In order to obtain information relating to the densities of allotropic modifications at absolute zero, measurements of the densities of diamond and graphite and of white and grey tin were made at a series of temperatures by a dilatometric method. The graphite was subjected to pressures of 1000 to 5000 atmospheres until the sp. gr. remained constant after repeated compression. The ratios of the specific gravities of diamond and graphite were found to be 1·585, 1·583, and 1·582 at 18°, −38°, and −164° respectively; those of white and grey tin, 1·266 and 1·274 at 78° and −164°. These numbers indicate that the specific volumes of the allotropic forms do not converge as the temperature falls.

H. M. D.

Associated Liquids. W. A. Kurbatoff and G. G. Eliséeff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1422—1425. Compare Abstr., 1909, ii, 117, 120).—In order to throw light on the abnormal values of the Ramsay-Shields constant given by certain apparently normal liquids, the authors have examined acetic anhydride and ethyl malonate in this connexion.

* also *Zeitsch. physikal. Chem.*, 1910, **71**, 385—400.

Acetic anhydride, for which Trouton's constant has the high value 22·9, is stated to give the normal value of the Ramsay-Shields constant, $K = d(\gamma M v^{2/3})/dt = 2 \cdot 129$, corresponding with a non-associated liquid. This value of K is confirmed by the authors' measurements, which give the mean result, $2 \cdot 12 \pm 3\%$, in open and closed vessels.

A whole series of esters are known which are normal as regards their thermal data and their values of Trouton's constant, but give abnormally high values for the Ramsay-Shields constant. This is also found to be the case with ethyl malonate, which gives values of K varying from 2·20 to 2·56.

The results obtained indicate that the value of the Ramsay-Shields constant varies for different homologous series. T. H. P.

Association of Glycerol. G. G. ELISÉEFF and W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1426—1427).—The values of the Ramsay-Shields constant for glycerol at various temperatures are as follows: 0·63 at 35·2—64·8°; 1·10 at 64·8—74·3°; 1·50 at 74·3—101·4°, and 1·20 at 101·4—123·4°, the alteration with temperature being almost identical with that exhibited in the case of ethylene glycol. It hence appears that the degree of association of glycerol is not less than that of ethylene glycol. These results give no reason for expecting that the molecule of sugar is a simple one. But if the sucrose molecules are associated, as indeed all molecules containing hydroxyl groups appear to be, then the laws of osmotic pressure derived from a study of sucrose solutions should be modified, and there is exhibited also a possibility of an explanation of the coefficient i other than that given by Arrhenius. T. H. P.

Adsorption of Ions. V. BOURNAT (*Compt. rend.*, 1909, **149**, 1366—1368).—Dilute solutions of binary electrolytes, excluding acids, have a higher surface-tension than water; acids, however, lower the surface-tension. The action of acids is probably due to the accumulation of hydrions in the superficial layer, giving the same effect as in the capillary electrometer. In support of this explanation it is shown that the addition of a hundredth molecular weight of potassium ferrocyanide to a litre of $N/5$-nitric acid increases the surface-tension to a considerable extent, whereas when added to a $N/5$-solution of a binary salt the increase is only very slight. Perrin has shown that multivalent ions diminish considerably the charge in a double layer, that is, that they accumulate in the surface layer, and in the experiment mentioned above they displace the hydrions and thus raise the surface-tension.

Comparing equimolecular solutions, the curve showing the relation between the molecular weights (abscissæ) of binary salts and the differences in the surface-tension (ordinates) of their solutions from that of water is a straight line. Monobasic acids also give a straight line lying below and parallel to that for the salts, the difference in the ordinates being 0·35 absolute unit for $N/10$-solutions. Sodium and potassium hydroxide raise the surface-tension of water, but not to the same extent as binary salts; in this case, also, a straight line is

obtained, the difference in the ordinates being 0·25 unit. These differences are apparently proportional to the molecular concentrations of the solutions. Assuming that the diminution in the surface-tension is due to the accumulation of ions in the surface layer, it is shown that the number (n) of ions absorbed per unit surface is given by the formula $n = \mu c^{\frac{1}{3}}$, where c is the concentration, and μ is a constant depending on the ion. This formula is analogous to the general adsorption formula of Freundlich. T. S. P.

Adsorptive Power of Hydroxides of Silicon, Aluminium, and Iron. III. Adsorption by Clay. II. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1909, **65**, 108—109; *Biochem. Zeitsch.*, 1909, **23**, 278—280. Compare Abstr., 1909, ii, 27, 551).—A property of a Fraustadt clay, the analysis of which is given, is to adsorb unsaturated hydrocarbons when it has imbibed its maximum quantity of water. It is, however, impermeable to saturated hydrocarbon. By means of this clay, the unsaturated hydrocarbons can be separated from the saturated in American petroleum. The hydroxides of clays of this description (silicon, aluminium, iron, and titanium) can adsorb organic substances containing oxygen, such as alcohol and acetone, but prevent the diffusion of organic substances, such as carbon disulphide, toluene, etc., and hydrocarbons which do not contain oxygen, with the exception of the unsaturated hydrocarbons. S. B. S.

Chemical Dynamics and the Colloidal State. I, II, and III. ALBERT REYCHLER (*J. Chim. Phys.*, 1909, **7**, 362—368, 497—510. Compare Biltz, Abstr., 1904, ii, 324, 392).—The experiments made by Biltz on the removal of arsenious acid from its solution by shaking with colloidal ferric hydroxide led to the conclusion that the amount of acid removed (x) was related to the amount remaining in solution ($a-x$) by the equation $x^5 = K(a-x)$. The phenomena were attributed to adsorption, but were not further investigated mathematically.

The amounts of ferric oxide used by Biltz in all his experiments were sufficient to form a normal arsenite with 1·4 grams of arsenious oxide, whereas the amount of arsenious oxide actually adsorbed never exceeded 0·824 gram, even when almost four equivalents were available. If a normal arsenite is produced, its concentration would be represented by $x/1{\cdot}4$, that of the free ferric hydroxide by $(1{\cdot}4-x)/1{\cdot}4$, and of the free arsenious oxide, $(a-x)/3$. Assuming that normal ferric arsenite is hydrolysed in the usual manner for a salt of a weak acid and a weak base, the equilibrium will be $(x/1{\cdot}4)^4 = K_3\{(1{\cdot}4-x)/1{\cdot}4\}^3(a-x)/3$, whence $K_3 = \sqrt[3]{x^4/(a-x)} \div (1{\cdot}4-x)$.

If, on the other hand, only two of the basicities of arsenious acid are exercised, the constant is $K_2 = \sqrt{x^3/(a-x)} \div (\frac{3}{2}\times 1{\cdot}4 - x)$.

It is shown that K_3 satisfactorily expresses Biltz's values up to the point where about one-half of the theoretically possible arsenious oxide is combined, and that above this K_2 gives a constant, pointing to the formation of some acid arsenite.

If the equivalent amount of arsenious oxide in Biltz's experiments is taken as 2·2 instead of 1·4, an even better constant (K_3) is obtained. It is not certain whether alumina has a similar affinity for arsenious oxide.

The author suggests that all so-called adsorption phenomena regulated by equations of the form $x^p/(a-x)=K$ may eventually be made amenable to the ordinary laws of chemical dynamics.

The experiments of Freundlich on the adsorption of various acids, etc., by blood-charcoal (Abstr., 1907, ii, 155, 939) can be considered as cases of chemical combination. Since, however, the basicity of charcoal is unknown, it is necessary to assume that 1 gram of charcoal is capable of combining with n-milli-equivalents of acid.

m-Grams of charcoal can therefore combine with mn-milli-molecules of a monobasic acid. If x milligram-molecules of acid be adsorbed, the degree of saturation of the charcoal is x/mn, and the unsaturated charcoal is $(mn-x)/mn$. If a is the initial concentration in the solution, $(a-x)$ is the final concentration. Assuming that the adsorption compound is hydrolysed like a salt of a weak acid with a weak base, $(x/mn)^2=K_1(mn-x)/mn\times(a-x)$, whence $K_1=(x/m)^2/(a-x)(n-x/m)$. By choosing a suitable value for n, a very satisfactory constant, K_1, can be obtained. The values are:

Acetic acid	$n=6$	$K_1=0·043$
Propionic acid	$n=5$	$K_1=0·139$
Dichloroacetic acid... ..	$n=6$	$K_1=0·21$
Formic acid	$n=8$	$K_1=0·020$
Butyric acid	$n=6$	$K_1=0·30$
Chloracetic acid	$n=4$	$K_1=0·33$
Benzoic acid	$n=4$	$K_1=24$
Sulphanilic acid	$n=5$	$K_1=0·21$

The strong acids, trichloroacetic acid and benzenesulphonic acid, do not give satisfactory constants; it is supposed that their adsorption compounds are not hydrolysed according to the same law. In the case of dibasic acids with only one active valency, $K=(x/m)^2/(a-x)(2n-x/m)$, whereas if both valencies be active, $K_2=\sqrt{(x/m)^3/(a-x)}\div(n-x/m)$.

With succinic acid both valencies are active: $n=10$ and $K_2=0·22$.

Citric acid acts as a tribasic acid: $K_3=0·16$ when $n=15$.

Bromine appears to follow the same adsorption law as monobasic acids, whereas methylamine follows a simple partition law. Adhesion, dissolution, etc., may in many cases superpose their effects on chemical adsorption.

The author's hypothesis is based on the theory that a large number of colloidal solutions may be considered as strongly basic or acidic salts.

For instance, the small proportion of hydrochloric acid which stabilises a solution of ferric hydroxide acts by combining with all the hydroxyls in turn, thus preventing the hydroxide from forming large complexes which on dehydration would be precipitated.

For every degree of dilution of the colloid sol there is a corresponding minimum of acid to prevent precipitation. All the known agents

for precipitating ferric hydroxide can be explained to act by disturbing the chemical equilibrium of acid, water, and ferric hydroxide.

Colloidal silica can be considered as a very acidic sodium silicate, and its properties can all be explained on chemical grounds.

The phenomena of cataphoresis and anaphoresis, the precipitation of colloids by electrolysis, may be due to the transfer of water to anode or cathode respectively, the colloid appearing to travel in the reverse direction. R. J. C.

Adsorption of Arsenious Acid by Ferric Hydroxide. WILHELM BILTZ (*J. Chim. Phys.*, 1909, 7, 570—574).—It is shown that Reychler's explanation (preceding abstract) of the author's observations relating to the absorption of arsenious acid by ferric hydroxide is untenable. This explanation is based on the assumption of the formation and hydrolytic decomposition of ferric arsenite.

New experiments have been made in which varying quantities of the hydroxide were shaken up with the same volume of a solution of arsenious acid of determined concentration. If z denotes the quantity of arsenious oxide taken up by m grams of the hydrogel, and x is the quantity which remains in solution, the observed results can be satisfactorily represented by the equation:

$$\log z/m = 0{\cdot}237 \log x + \log k.$$

From this the author concludes that the removal of arsenious acid from the solution by the ferric hydroxide is a pure adsorption phenomenon. H. M. D.

Thermodynamics of the Capillary Layer. GERRIT BAKKER (*Zeitsch. physikal. Chem.*, 1909, 68, 684—692).—A mathematical paper. The author indicates certain errors very often committed in applying thermodynamical considerations to the capillary layer.

When the capillary layer is considered by itself, instead of the usual equation: $dQ = d\epsilon - Hds$ (where dQ is the heat absorbed in varying the surface, $d\epsilon$ is an energy difference, H is the surface-tension, and ds the change of surface), the equation $dQ = d\epsilon + p_N dv - Hds$ must be used, where p_N is the vapour pressure, and v the specific volume of the capillary layer. The last equation is the correct expression for the specific heat of the capillary layer per unit of mass. Nothing is known as to the variation of this specific heat with temperature.

The energy equation obtained when a vessel filled with liquid, vapour, and the capillary layer as transition layer is considered, differs from that deduced for a thin sheet. G. S.

Relationship between Physical Properties of Solutions. I. Density and Electrical Conductivity of Aqueous Solutions of Salts. ADOLF HEYDWEILLER (*Ann. Physik*, 1909, [iv], 30, 873—904).—From an examination of the data for a large number of aqueous solutions of electrolytes, it is shown that a connexion exists between the density of a solution and that of the solvent, which can be expressed by the equation $\Delta = B + (A - B)i$. In this equation, Δ denotes the percentage change in density per gram-equivalent of the dissolved

electrolyte, i is the ratio of the equivalent conductivity of the given solution to the conductivity at infinite dilution, and A and B are constants. A and B represent respectively the percentage changes in density which are caused by one gram-equivalent of ionised and non-ionised electrolyte; $A-B$ represents the influence of ionisation on the density of the solution. The values of A and B are tabulated for a number of electrolytes.

For certain electrolytes, the values of B indicate that the volume of the undissociated electrolyte in solution is the same as that of the salt in the solid state. In other cases, changes in volume take place on solution. The contractions which are found in the case of salts which form hydrates in the solid state indicate that hydrated molecules are also present in the aqueous solutions.

Ionisation of the electrolyte is always accompanied by an increase in density, and this is found to become greater as the sum of the mobilities of the constituent ions increases. The observed contraction is shown to be probably due to a diminution in the volume of the water.

The values of A exhibit additive relationships, and ionic moduli are calculated, by means of which it is possible to calculate the influence of the ionised portion of any electrolyte on the density of its aqueous solution.

Certain electrolytes are abnormal, in that they do not agree with the relationship $\Delta = B + (A - B)i$. The anomalous behaviour is traced in some cases to the formation of complex ions in the more concentrated solutions, and to the large affinity of the dissolved salts for water.

H. M. D.

Condition of Equilibrium between a Dilute Solution and the Pure Solvent Separated by a Semi-permeable Diaphragm or by the Vapour of the Solvent. GIOVANNI GUGLIELMO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 536—544).—Making use of two relations which were obtained by van der Waals (see *Die Continuität des flüssigen und gasförmigen Zustandes*), and which express the condition of equilibrium of a large number of molecules (considered as material points) in perpetual motion and attracting one another, the author derives (1) in two forms, the condition of equilibrium of the molecules of a chemically homogeneous liquid, and (2) the equilibrium conditions for a chemically heterogeneous liquid—solvent and solute; (3) the condition of equilibrium between pure solvent and solution separated by a semi-permeable surface. With the aid of the results thus obtained, the following questions are discussed: independence of the molecular attraction on the mass of the molecules, and a hypothesis on the nature of this attraction; causes of the lower vapour pressure of solutions compared with the solvents, and of the equality of vapour pressure for equimolecular solutions; influence of the curvature of the surface of a liquid on its vapour pressure.

T. H. P.

Binary Mixtures and Concentrated Solutions. Remarks on Dolezalek's Paper. THOMAS S. PATTERSON (*Zeitsch. physikal. Chem.*, 1909, **67**, 572—574. Compare Dolezalek, Abstr., 1909, ii, 22).—It is

shown that the theoretical densities of mixtures of chloroform and acetone calculated by Dolezalek are incorrect, as they were obtained by multiplying the respective densities of the components by the molecular fraction of the component in the mixture instead of by the usual method. The observed density of a particular mixture of chloroform and acetone only differs very slightly from the theoretical value; the deviation is only one-ninth of that given by Dolezalek, and the conclusions of the latter investigator therefore require revision.

G. S.

Existence and Properties of Disperse Systems in the Region Separating Colloidal and Crystalloidal Solutions. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 6, 318—325. Compare Abstr., 1909, ii, 389).—Experiments are described which show that the absorption of light by a gold hydrosol increases as the size of the colloidal particles increases. By raising the temperature of a ruby-red hydrosol or by the addition of electrolytes, the particles were caused to coagulate, and measurements of the colour intensity showed a gradual increase in the absorptive capacity of the hydrosol. The addition of a non-electrolyte was found to be without influence on the absorption.

By the reduction of a solution of gold chloride by means of hydrazine in presence of gelatin (free from electrolytes) as protective colloid, gold hydrosols consisting of extremely small particles can be obtained. The intensity of the colour of the hydrosol obtained in this way is much smaller than that of the hydrosol obtained under similar conditions in the absence of the protective colloid. The action of this consists in reducing the rate of coagulation of the hydrosol, and it is shown that the activity of the gelatin is approximately proportional to its concentration.

Gold hydrosols prepared in different ways exhibit considerable differences in respect of the position and the intensity of the absorption maximum. This is found to depend on the size of the colloidal particles. As the size diminishes, the absorption maximum shifts towards the region of smaller wave-lengths. For the most highly disperse hydrosols this maximum is in the ultra-violet, and approximates to the position of the maximum for a solution of gold chloride.

H. M. D.

Theory of Colloids. JACQUES DUCLAUX (*J. Chim. phys.*, 1909, [vii], 405—446. Compare Duclaux, Abstr., 1909, ii, 303; Malfitano, *ibid.*, 473; Pappada, *ibid.*, 473).—The author develops the theoretical ideas already put forward by him into a complete theory of colloids. The physical theory, which postulates that the stabilising ions in a colloidal solution are permanently combined with the colloid particles, and that the whole osmotic pressure is due to colloid particles acting as molecular units, fails to explain the difference in properties when one stabilising ion is substituted for another. According to the chemical theory put forward by the author, colloid particles are very large multivalent ions forming salts with the stabilising ions which surround them, but which are capable of super-adding their osmotic

pressures, conductivities, etc., to that of the nucleus granules or micella (compare Reychler, this vol., ii, 105). The degree of ionisation will vary with the nature of the stabilising ion. For instance, ferric hydroxide stabilised with sulphuric acid has a much lower osmotic pressure than the same colloid stabilised with hydrochloric acid.

It is shown that if the colloidal micella is assumed to be exactly comparable to an ionisable salt, the osmotic pressures calculated from the conductivities and ionic mobilities of the solutions are about double the experimental osmotic pressures. The measurements were all made on solutions with a very pure intergranular liquid (compare, however, Malfitano, *loc. cit.*), and a small correction was subtracted for the conductivity of the intergranular liquid. The ionic mobilities of the colloid granules were determined by passing a direct current through the solution and afterwards analysing the liquids in the anode and cathode chambers, it being assumed that no transference of water had occurred. The ultramicroscope is not available here, because colloids with an appreciable osmotic pressure are so small as to be almost invisible.

When a colloidal solution is dilute, the micella are so widely separated that the ions surrounding each one are never attracted from it, but the whole comprises a stable, almost neutral sphere. On establishing an electric field, the ions all crowd to one side of the sphere and the parent granule to the other. Since the voltages required for electrolysis are small, it follows that only a few of the ions become detached. When the solution is concentrated, the micella approach each other, and ultimately their neutral spheres intersect. Each micella will then facilitate the ionisation of its neighbours, a kind of Grotthus's chain being set up. It follows that as a colloidal solution is concentrated, its "molecular" conductivity increases. This is shown to be the case with ferric hydroxide and gum arabic. The degree of ionisation of a colloid does not mean the proportion of granules ionised, but the average extent to which each granule is ionised. Knowing the number of stabilising ions, the degree of micella ionisation can be calculated. It varies in the author's experiments from 0·008 in copper ferrocyanide to 0·88 in gum arabic. If the intergranular liquid contains electrolyte, this must have an ion in common with the micella, and will influence its ionisation.

When the degree of ionisation of the micella, the ionic velocity, and the viscosity are known, the radius of the micella can be calculated with the aid of Stokes' theorem. This varies from $0·55\mu\mu$ in tungstic acid to $5·2\mu\mu$ in Prussian-blue, the number of free ions per micella being 2·9 and 24 respectively.

These values are in accord with the relative retention of the colloids by collodion, and are also of the same order as the radius, $<1\mu\mu$, found by Zsigmondy for colloidal gold particles.

The molecular weights of the colloids, calculated from their micella radii are: tungstic acid 1900, thorium hydroxide 7000, gum arabic 16,000, ferric hydroxide 115,000, copper ferrocyanide 700,000, Prussian-blue 1,000,000.

The neutral sphere probably has a radius about ten times that of

the micella, that is to say, on an average an ion does not move further than $10\mu\mu$ from the micella.

Direct measurements have been made of the osmotic pressures of ferric hydroxide, copper ferrocyanide, Prussian-blue, thorium hydroxide, gum arabic, and caramel with collodion membranes. The results confirm those obtained by the filtration method (Abstr., 1909, ii, 303), and clearly show that the osmotic pressure of a colloid increases more rapidly than the concentration. In very dilute solution each micella with its ions complete acts osmotically as one molecular unit.

As the concentration increases, it may attain by splitting off of ions an osmotic value of 8 or more. R. J. C.

General Equation of State. KARL DRUCKER (*Zeitsch. physikal. Chem.*, 1909, **68**, 616—636).—A theoretical paper. A general equation of state is deduced on the assumption that the gas laws hold for gases and pure liquids in general, and that the deviations are to be accounted for on purely chemical grounds, that is, on the formation of complex molecules (polymerides). On this basis the general gas equation $pv = RT.\Sigma n$ leads to the equation: $p/RT = \Sigma n/v = \Sigma c = c_1 + c_2 + c_3 + \ldots$ (1), where $\Sigma c = c_1 + k_2c_1^2 + k_3c_1^3 + \ldots$ In this equation c_1, c_2, etc., represent the respective partial concentrations of the simplex and complex molecules; k_1, k_2, etc., represent the respective equilibrium constants, and the other symbols have the usual significance. It is assumed in deducing this equation that equilibrium between simple molecules and their polymerides is established instantaneously.

In equation (1) the coefficients are necessarily positive, and it appears at first sight as if it applies only to cases where the compressibility is too great. Although this difficulty can theoretically be got over, it has been considered advisable to insert a volume correction (analogous to that of van der Waals) in equation (1). The equation is then tested by application to the data for ethyl ether, methyl alcohol, and other vapours given by Ramsay and Young and others, and simplified forms of it are found to give satisfactory results.

The application of these considerations to liquids leads to the conclusion that a liquid under ordinary conditions consists of a dilute solution of unimolecules in complex molecules. The fact that this result is in apparent conflict with the method of determining the molecular complexity of liquids due to Eötvos-Ramsay-Shields, based on surface-tension measurements, is not regarded as an insuperable objection, as the method in question has no purely thermodynamic basis. The author considers that liquids, such as water, usually regarded as complex, are really comparatively simple.

Provisional suggestions are made for determining the partial concentrations in liquids. G. S.

Demonstration of the Phase Rule. R. BOULOUCH (*Compt. rend.*, 1909, **149**, 1377. Compare Abstr., 1909, ii, 802).—The author maintains his criticisms of Müller's demonstration of the phase rule,

pointing out that Müller has confused three things which are essentially distinct, namely: (1) the actual changes taking place in a system not in equilibrium; (2) the virtual changes which one imagines to take place in a system in equilibrium; (3) the atomic interchanges occurring, according to the atomic theory, in a system in equilibrium.

T. S. P.

Invariant Systems and the Regularity of Composition of Certain Eutectics. Alex. Gorboff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1241—1300).—The author discusses the phase rule and the composition of eutectic mixtures, a large number of examples from the work of various investigators being considered. The principal results arrived at are as follows.

One of the fundamental propositions of chemical mechanics is that the laws by which material systems are characterised are determined, not by the number of their components, but by the number of effective degrees of freedom.

Examination of the compositions of eutectics formed by the elements and by chemical, "molecular," and "complex" compounds shows that the composition of any eutectic corresponds with a chemical compound formed by the elements occurring in the eutectic, which may hence be expressed by a chemical formula with rational indices. So that eutectics obey not only the law of constant composition, but also the law of multiple proportions.

Not only may the composition of a eutectic formed by two independent components capable of giving chemical compounds melting without decomposing be expressed by a chemical formula, but this formula is often constructed according to a simple rule—equal masses of one of the two components being distributed in both solid phases of the eutectic. Thus, if the two components, A and B, form the compounds $A+xB$ and $A+yB$, melting without decomposing, then the eutectic between A and $A+xB$ is expressed by the formula $2A+xB$, and that between $A+xB$ and $A+yB$ by the formula $(yA+xyB)+(xA+xyB)$ or $(x+y)A+2xyB$, and so on. Excluding the limiting eutectics answering to the general formula, $2A+xB$, in all the others, expressed, for example, by $(x+y)A+2xyB$, in both solid phases that independent component is distributed in equal masses which possesses the more basic chemical character. The latter in the eutectics formed by crystallo-hydrates of sulphur dioxide, hydrogen chloride, hydrogen iodide, nitrogen pentoxide, copper nitrate, magnesium chloride, ferrous nitrate, and ferric chloride is water, and in the metallic eutectics the more alkaline metal.

In every case where a chemical compound of two components does not melt without decomposing, but exhibits a transition point below the melting point, its solubility in one of the components is lower, sometimes very considerably lower, than is required by the above rule; in such cases, this component consequently occurs in excess in the eutectic.

For the large numbers of experimental data from which these conclusions are drawn and for references given, the original must be consulted.

T. H. P.

Influence of Centrifugal Force on the Equilibrium of Chemical Systems. A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1306—1308).—When a concentrated solution of cadmium iodide is subjected to centrifugalisation in a tube closed with a cork, a brown precipitate containing cadmium and iodine is deposited, whilst aqueous hydrogen iodide under similar conditions gives a deposit of iodine. The author's results seem to indicate that the cork acts as a catalyst.

Also, centrifugalisation of solutions of ferric chloride and mercurous nitrate produces a marked increase in the electrical conductivity of the solutions, the increased values persisting after removal of the centrifugating force and mixing of the liquids. Since all the compounds used in his experiments are readily decomposed by water, the author suggests that such decomposition may occur to a slight extent, and that one of the products of the decomposition, being the heavier, may be readily removed from the sphere of action by the centrifugalisation. Thus, with ferric chloride, the ferric hydroxide formed by the hydrolytic dissociation would pass to the periphery of the centrifuge, and thus permit of the hydrolysis of further quantities of ferric chloride; the hydrochloric acid formed by the hydrolysis would cause the increased conductivity observed.

Colloidal solutions of antimony sulphide and ferric hydroxide deposit precipitates when subjected to centrifugalisation. T. H. P.

Chemical Affinity. III. Solution-affinity of Binary Systems. II. Sulphuric Acid and Water. J. N. BRONSTED (*Zeitsch. physikal. Chem.*, 1909, **68**, 693—725).—The theoretical conclusions discussed in the previous paper (compare Abstr., 1909, ii, 29) are now tested by application to the system sulphuric acid-water.

The heat of admixture of sulphuric acid and water has been determined over the whole range of concentrations, and as large amounts of the substances were used, the results are probably very accurate; they are represented in tabular form in various ways. The heat of formation of 1 mol. of monohydrate is 6710 cal. The m. p. of pure sulphuric acid on the hydrogen scale is 10·49°. The results obtained are in good agreement with those of Pfaundler and of Pickering (Trans., 1890, **57**, 94), but not with those of Thomsen (*Thermochemische Untersuchungen*); it is probable that Thomsen's "pure" acid contained a little water. From the results, the differential curves for the heats of admixture are determined by means of the equations given in the earlier paper.

The solution-affinity of the components throughout the whole range of concentrations is then determined from the combined results of *E.M.F.* measurements, of vapour-tension measurements, and of freezing-point determinations. The reaction, the *E.M.F.* of which has been determined, is the formation of sulphuric acid by the reduction of mercurous sulphate by hydrogen, the cell being built up as follows: $H_2 \mid H_2SO_4 \mid Hg_2SO_4 \mid Hg$. Measurements have been made between 15° and 80° with varying proportions of acid, and the affinity is calculated from the results by means of the Helmholtz equation in the usual way.

As regards vapour-pressure measurements, the results of Tammann (*Zeitsch. physikal. Chem.*, 1888, **2**, 42) at 100°, and of Dieterici (*Ann. Phys. Chem.*, 1893, [ii], **50**, 47) at 0°, have been supplemented by measurements at 20° and 30° with a special form of apparatus.

In connexion with the calculation of solution-affinity from freezing-point determinations with the help of thermal constants, it has been found that the heat of fusion of sulphuric acid is $2485 + 6 \cdot 1t$ calories per mol., and that of the monohydrate, $4290 + 18 \cdot 8t$ calories. From these results the differential solution-affinity curves for water and acid respectively have been obtained, and for comparison are plotted on the same diagram with the corresponding curves for the heat of admixture. The forms of the curves are very different from the ideal type, due to chemical reaction between water and acid.

As regards the sulphuric acid curve, A, the solution-affinity is greater than U, the heat of admixture, for $x = 1$ (x is the molar proportion of acid in the mixture); the curves intersect at $x = 0 \cdot 53$, where $A = U = 1400$ cal., beyond which the A-curve is lower than the U-curve, until they again intersect at $x = 0 \cdot 006$, when $A = U = 17,000$ cal. For water the affinity and heat of reaction curves practically coincide for concentrations between 0·1 and 0·3.

The values found are throughout in accord with the general thermodynamic equation: $A - U = T \times dA/dT$ (where the symbols have the usual significance). G. S.

Affinity of Sodium Phosphate for Water. PAUL TH. MULLER (*J. Chim. Phys.*, 1909, **7**, 534—539).—The theorem recently published by Nernst (Abstr., 1907, ii, 153) correlating affinity with temperature in condensed systems is applied to the affinity of sodium phosphate for water.

The affinity of the hydrate, $Na_2HPO_4,12H_2O$, for its water is given by the formula $A = 1 \cdot 985 T \log_e f/f'$ cal., where f and f' are the vapour pressures of pure water and hydrate respectively at temperature T. Nernst's equation gives $A = Q_0 - \alpha T^2 - \beta T^3/2$, where Q_0 is the heat of hydration at absolute zero. The values of A in the first formula are calculated from Frowein's measurements of the vapour pressure of the hydrate between 6·8° and 27·00°. If $Q_0 = 1200 \cdot 58$ cal., $\alpha = 0 \cdot 0119827$, and $\beta = 0$, Nernst's formula gives values agreeing with Frowein's within 0·35%. The heat of hydration at any temperature is equal to $Q_0 + \alpha T^2 + \beta T^3$. Hence the heat of hydration of sodium phosphate at 18° should be 2215·3 cal., whereas Thomsen and Pfaundler obtained the values 2234 cal. and 2244 cal. by direct measurements. When the affinity for water (A) is zero, $(Q - \alpha T^2) = 0$, whence $T = 316 \cdot 5°$ abs. It follows that at 43·5° the phosphate becomes anhydrous. Extrapolation of Frowein's results indicates that at about this temperature the vapour pressure of the phosphate begins to exceed that of water. R. J. C.

Chemical Kinetics. OTTO SACKUR (*Zeitsch. Elektrochem.*, 1909, **15**, 865. Compare Trautz, Abstr., 1909, ii, 651).—Trautz's equations for the velocity of a reaction are obtained, essentially, by dividing the well known equation $d \log K/dT = Q/RT^2$ into the two equations: $d \log k_1/dT = q_1/RT^2$ and $d \log k_2/dT = q_2/RT^2$, where k_1 and k_2 are the

velocity constants of the two opposite reactions, and q_1 and q_2 are the sums of the heats of formation of the molecules taking part in them. The equations are then integrated by means of Nernst's theorem. The author points out that these partial equations are not necessarily correct, because a pair of equations of the form $d \log k/dT = q/RT^2 + \phi(T)$, where $\phi(T)$ is any function of the temperature, would equally, when subtracted from each other, give the original equation. The assumption that $\phi(T) = 0$, although possible, is not necessarily true. T. E.

Temperature-coefficient of Chemical Reaction Velocities. IV. Addendum. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, **68**, 637—638. Compare Abstr., 1908, ii, 924; 1909, ii, 557; this vol., ii, 24).—Sackur's adverse criticisms (compare preceding abstract) of the author's work, in so far as they are new, are not valid. G. S.

Residual Affinity and Additivity. Part II. WALTER PETERS (*Ber.*, 1909, **42**, 4826—4836).—The observations on the union of ammonia with various salts (compare Abstr., 1908, ii, 937) have been further extended. In the platinum complex salts, the additive power (for ammonia) cannot be considered as an additive property of the component salts. A consideration of the additive ammonia compounds of copper and cadmium platinichlorides shows that the complex salt either adds on ammonia as a whole, or else the anion and cation each exert their own particular residual affinity. The compounds of copper and cadmium behave very similarly to each other, as also do the compounds of bivalent manganese and zinc.

Metals belonging to the same periodic group show the same or very similar behaviour. Uranium tetrachloride has a greater additive power for ammonia than has uranyl chloride. Replacement of one halogen by another has no influence on the residual affinity.

Werner's co-ordination number six, or a multiple thereof, holds for half of the salts mentioned in this and the previous communication.

Many salts which are hygroscopic no longer show this behaviour after the addition of ammonia; the fact that a salt is hygroscopic therefore depends on the exertion of subsidiary valencies.

The following table gives a summary of the results at the ordinary temperature: I giving the number of mols. of ammonia absorbed, and II the number retained after evacuation.

	I.	II.
Calcium platinichloride	12	6
Barium platinichloride	6	5
Zinc platinichloride	11	7
Manganese platinichloride	11	7
Copper platinichloride	18	6
Cadmium platinichloride	18	6
Cobalt platinichloride	12	10
Nickel platinichloride	12	10
Sodium platinochloride	4	3
Sodium platinibromide	6	5
Platinous iodide	5	4
Platinic chloride	6	5
Platinic bromide	6	5
Palladious chloride	5	4
Sodium palladiochloride	5	4
Ammonium palladiochloride	5	4
Palladious iodide	6 (at 0°)	2
Rhodium chloride	4	3
Ruthenium chloride	3	3
Ruthenium bromide	3	2
Cuprous chloride	3	1
Cuprous iodide	3	0
Silver nitrate	3	2
Chromous chloride	6	3
Uranium tetrachloride	3	3
Uranyl chloride	2	1
Manganous chloride	6	2
Manganous iodide	6	5 ?
Manganous sulphate	6	2

Neither hydrogen chloride nor phosphine combines with any dry inorganic salt. Acetylene is absorbed only by cuprous chloride. Ethylene gives no additive products; its absorption by ferrous and platinous chloride in ethereal or hydrochloric acid solution only takes place when these chlorides are formed by reduction of the corresponding ferric and platinic chlorides. Carbon monoxide was not absorbed by any of the salts investigated under the particular conditions of experiment. T. S. P.

Eder's Solution. I. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1909, 7, 409—441).—The rate of the photochemical reaction between mercuric chloride and ammonium oxalate in aqueous solution is increased by ceric salts and potassium ferricyanide, and decreased by cupric salts, potassium tin chloride, and many organic colouring matters. Potassium iodide in small quantity accelerates the reaction, but when this is present in excess, the velocity of the reaction diminishes.

In order to obtain information relative to the nature of the catalytic effect, the author has examined the behaviour of chlorine, potassium permanganate, and more especially ferric salts. In the case of chlorine the catalytic phenomenon is traced to the inducing effect of the reaction between chlorine and ammonium oxalate on that between the mercuric salt and the oxalate. The action of potassium permanganate is found to be accompanied by a period of induction, during which the permanganate is reduced to a manganic salt, which then accelerates the photochemical change. The mode of action of this is in all probability similar to that of ferric salts.

The numerous experiments made on solutions containing iron salts show that the catyltic effect is very largely dependent on the amount of oxygen which is present. In the absence of oxygen, the catalytic process can be resolved into two stages, in one of which the rapid photochemical reduction of ferric oxalate is involved, whereas the other consists in the inducing effect of the oxidation of the ferrous oxalate formed in the photochemical reduction process. In presence of oxygen, the process is complicated by reason of the action of the oxygen on the reduced ferric salt.

In support of this view it is found that the rate at which mercurous chloride is precipitated from a solution containing a given amount of ferrous salt increases as the amount of oxygen in the solution diminishes. For a given quantity of ferrous salt, the total amount of mercurous chloride precipitated increases as the oxygen concentration diminishes. Ferric salts diminish the rate of the reaction. For a given ratio between ferric and ferrous salts, the retarding effect increases rapidly with the total amount of iron in the solution. These observations are in accord with the fact that maximum photo-sensitiveness is obtained for a particular iron concentration. Since the retarding action of ferric salts increases when the amount of oxygen in the solution diminishes, the iron concentration corresponding with maximum sensitiveness diminishes with the oxygen concentration.

The rate of precipitation of mercurous chloride from Eder's solution

is recommended as a means of estimating small quantities of dissolved oxygen. H. M. D.

Vacuum Correction of Weighings Applied to Atomic Weight Determinations. PHILIPPE A. GUYE and N. ZACHARIADÈS (*Compt. rend.*, 1909, **149**, 1122—1123. Compare Abstr., 1909, ii, 989).—The authors have determined previously the magnitude of the error made in reducing weighings to vacuum values, through the presence of condensed air on the surface of the substance. These calculations have now been revised after taking into account another source of error. The new numbers, together with the results of fresh determinations for other common substances, are given in tabular form. The results were obtained by weighing a flask in air (*a*) exhausted of air, (*b*) full of air, (*c*) containing air and the substance, (*d*) containing the substance only.

The apparent weight of the salt in air is reduced to the vacuum value by the usual method, and compared with the "actual weight in vacuum" given by $(d-a)-p$, where p is the loss of weight in the air of the standard weights. A further correction should be made for the air condensed on the surface of the standard weights.

The "actual weight in vacuum" was in each case found to be higher than the calculated value, the difference ranging from 1 mg. in the case of silver bromide to 25 mg. in the case of sodium chloride per 100 grams. In the case of silver, however, the numbers were the same. W. O. W.

The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], **19**, 1—25).—On the assumption that positive and negative electrons are associated in pairs, and are revolving round one another in such a way that each pair has an average electric moment, it follows that if these moments are similarly directed, the atom as a whole will have an electric moment, and can be investigated as a uniformly electrised sphere. It is shown that the internal electric fields cause atomic vibrations, and that the atomic vibrator can be regarded as the single electron which is involved in the explanation of the Zeeman effect. The common constant which appears in Rydberg's formulæ for the series lines of many elements is discussed in terms of this conception of the atomic vibrator. An explanation of dielectric capacity in terms of the electron theory is given, and it is shown that Balmer's formula relating to spectral structure can be interpreted on a kinematical basis. H. M. D.

Molecular Diameters. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], **19**, 25—26).—On the basis of the value $2{\cdot}77 \times 10^{19}$ obtained by Rutherford for the number of molecules in 1 c.c. of a gas under standard conditions, the author has recalculated a series of molecular diameters with the following result: H_2 2·17, He 1·02, CO 2·74, C_2H_4 3·31, N_2 2·95, NO 2·59, O_2 2·71, A 2·66, CO_2 2·90, N_2O 3·33, Cl_2 $3{\cdot}76 \times 10^{-8}$ cm. H. M. D.

Liquid Extraction with the Aid of Soxhlet's Apparatus. TADASU SAIKI (*J. Biol. Chem.*, 1909, 7, 21—22).—A modification of Soxhlet's apparatus is described and figured for the extraction of liquid material with ether. W. D. H.

Apparatus for Evaporating Ethereal Solutions. GILBERT P. GIRDWOOD (*Analyst*, 1909, 35, 16).—The one end of an inverted siphon has the shape of a funnel, and the other end projects several inches below the level of the ethereal solution to be evaporated. The watch-glass containing this is placed under the funnel-shaped opening, and by applying suction to the long arm, the ether vapour siphons over, and the residue is finally deposited in a small space in the centre of the watch-glass.

The same means may be adopted for concentrating an ethereal solution in a test-tube or beaker by gradually lowering the funnel of the siphon as the ether evaporates. L. DE K.

Inorganic Chemistry.

Condition of Dissolved Iodine. PERCY WAENTIG (*Zeitsch. physikal. Chem.*, 1909, 68, 513—571. Compare Beckmann, Abstr., 1907, ii, 340).—The investigation of solutions of iodine in a large number of solvents has led to the conclusion that in all the solutions iodine is partly combined with the solvent according to the reversible equation : $SoI_2 \rightleftarrows So + I_2$ (So = solvent) ; for the violet solutions, the spectra of which approximate to that of iodine vapour, the amount of combination is much less than for the brown solutions.

These conclusions are mainly based on spectroscopic observations, and, in particular, the effect of change of temperature on the spectra has been fully investigated. On heating the violet solutions, the absorption band becomes displaced towards the red end of the spectrum, in other words, towards that of iodine vapour, and is displaced in the opposite direction on cooling. The spectra of many of the brown solutions tend to become permanently altered on heating, a result which speaks in favour of considerable association between iodine and solvent. The view that there is only a difference in degree between violet and brown solutions is further supported by the fact that brown solutions in thiophen and in sulphur dioxide become violet on heating, and regain the original colour on cooling.

The conclusion to be drawn from the displacement of the equilibrium with temperature that the heat of formation of the compound must be positive, is supported by observations on the effect of temperature on the solubility of iodine, and on its heat of solution in different solvents. Although the heat of solution is negative in all the solvents examined except pyridine, the heat absorption is much less for brown than for violet solutions. Moreover, cryoscopic investigations with iodine and a "solvent" dissolved together in an indifferent solvent show that the

depression is so much the smaller the greater the degree of combination according to the above considerations (compare Hildebrand and Glascock, Abstr., 1909, ii, 225). A compound with pyridine, of the formula PyI_2, has been isolated.

The influence of dilution on the absorption spectra has been measured for two kinds of light, and it was found that, contrary to the requirements of the law of mass-action, the ratio of the absorption for both kinds of light increases with dilution. This is probably connected with ionisation of the additive compound, as many of the solutions have a considerable molecular conductivity, which increases with the dilution.

The observations on the nature of the absorption bands, and of their displacement with temperature, are satisfactorily accounted for on the assumption that there is a maximum of absorption for the additive compound in the ultraviolet, and that the absorption due to the compound is more or less affected by the absorption band due to free iodine.

The partial vapour pressures of the components in boiling solutions of iodine in ether, carbon disulphide, chloroform, carbon tetrachloride, and benzene have also been determined, and the results, considered from the point of view due to Dolezalek (Abstr., 1909, ii, 22), support the above conclusions. Even at the boiling point there is considerable association between iodine and solvent in the brown solutions.

The molecular freezing-point depression for carbon tetrachloride is 299. G. S.

Production of Ozone by Ultraviolet Light. EDMOND VAN AUBEL (*Compt. rend.*, 1910, **150**, 96—98).—The following correction should be made in the previous paper (this vol., ii, 28). In the experiments where water was used to absorb the ozone produced, the resulting solution contains hydrogen peroxide, the presence of which was detected by its action on a photographic plate. The presence of hydrogen peroxide in the water proves the formation of ozone in the air by the action of the ultraviolet light. T. S. P.

Dissociation Isotherms of Sulphur between 300° and 850°. GERHARD PREUNER and W. SCHUPP (*Zeitsch. physikal. Chem.*, 1909, **68**, 129—156).—By means of the quartz-glass manometer described by Abegg and Johnston (Abstr., 1908, ii, 157), the authors have determined the density of sulphur vapour at nine temperatures between 300° and 850° and within wide limits of pressure. The results cannot be reconciled with the assumption that only S_8 and S_2 molecules are present, but indicate that above 30 mm. pressure only S_8, S_6, and S_2 molecules are present. At pressures lower than 30 mm. it is possible that S_1 molecules are also contained in the vapour.

From the displacement of the different equilibria with temperature, it is calculated that in the reaction $3S_8 = 4S_6$, 29,000 calories are absorbed, and in the other reaction, $S_6 = 3S_2$, 64,000 calories are absorbed. Similarly, the change of gaseous S_8 to $4S_2$ absorbs 95,000 calories. From the most trustworthy results on the variation of the vapour pressure of sulphur with the temperature, it is calculated that the heat

of vaporisation, 8S[solid] ⟶ S_8(gaseous), is 20,000 calories, hence for the reaction $8S_1$[solid] ⟶ $4S_2$(gaseous), 115,000 calories are absorbed. Otherwise expressed, it requires about 115,000/4 = 28,800 calories to transform 64 grams of solid sulphur into gaseous S_2.

On the assumption that S_6 is identical with $S\mu$, the modification of sulphur insoluble in carbon disulphide, the proportion of $S\mu$ in saturated sulphur vapour is calculated from the density results at different temperatures, and compared with the values determined directly by Gal (Abstr., 1893, ii, 455) and by Kruyt (Abstr., 1908, ii, 1028). The authors' results are in excellent agreement with those of Gal, but not with those of Kruyt. G. S.

Action of Hydrogen on Sulphur or Selenium in Presence of Another Element. HENRI PÉLABON (*J. Chim. Phys.*, 1909, **7**, 447—463).—Excess of pure sulphur or of sulphur containing less than 2/3 atomic proportion of arsenic when heated at 610° in hydrogen gives a gaseous mixture containing about 98% of hydrogen sulphide. When the proportion of arsenic is increased until the sulphur is saturated at approximately the composition SAs_2, the amount of hydrogen sulphide decreases regularly to 78%. Further addition of arsenic, which remains as a separate phase, does not decrease the amount of hydrogen sulphide produced. The uniphase solutions of arsenic in sulphur give a greater proportion of hydrogen sulphide the less the pressure of hydrogen, but mixtures containing a free arsenic phase always give 78% of hydrogen sulphide.

The results obtained with mixtures of arsenic and selenium are analogous, but the proportions of hydrogen selenide are in all cases much lower.

Addition of selenium or tellurium to mixtures of sulphur and arsenic promotes the formation of hydrogen sulphide, but to a less extent than an equivalent amount of sulphur itself.

Selenium produces a similar effect on mixtures of sulphur and antimony, but tellurium is here without influence.

The addition of antimony to sulphur makes no change at first in the amount of hydrogen sulphide (98%), but when 43—90 atoms of antimony are present per 100 of sulphur, the liquid consists of two phases, antimony sulphide saturated with antimony, and antimony saturated with its sulphide. Whilst these two phases are present, the proportion of hydrogen sulphide produced is about 60%. With larger proportions of antimony, the hydrogen sulphide rapidly decreases towards zero.

The phenomena with mixtures of selenium with antimony, bismuth, tin, and thallium are similar to those obtained with selenium and arsenic. Silver and copper, on the other hand, which form stable selenides solid at the temperature employed, entirely prevent the formation of hydrogen selenide when their proportions exceed Ag_2Se and Cu_2Se. R. J. C.

Preparation of Colloidal Solutions of Selenium. ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 544—551).—In preparing colloidal solutions of selenium by the method of Müller

and Nowakowski (Abstr., 1906, ii, 18), the author finds that, at the same time as a red coloration forms in the liquid near the cathode, the current intensity exhibits a continuous increase which begins immediately the circuit is closed. If the liquid in the cell is shaken, the current intensity falls sharply, but rises to the original value as soon as the shaking ceases, and then continues to rise to a certain limiting value, which may be as much as ten times the initial current; if the liquid is kept continually agitated, a longer time is required for the current to increase to the limiting value.

By this method, if the duration of the current is sufficient to allow of the liberation from the cathode of more than about 0·24 gram of selenium per litre of water present, a deposit of red selenium begins to form at the bottom of the cell. If a solution prepared in this way is filtered and subjected to an *E.M.F.* of 40 volts between polished platinum electrodes, the current increases gradually from about 40 milli-amperes at the beginning to about 60 milli-amperes after two hours; if the current is interrupted for some time and then re-applied, the initial value is again about 40 milli-amperes, and the same gradual increase takes place. The increase of current seems to be due to a diminution in the resistance of the liquid present in the cell.

When a dilute solution of selenious anhydride is electrolysed with platinum electrodes, the phenomena observed vary with the *E.M.F.* employed. With 3 volts, a red deposit forms on the cathode, and the current gradually falls; with 17 volts, the deposit forms almost instantaneously and increases in thickness, the current remaining sensibly constant; whilst with 48 volts, the current gradually increases, whilst the liquid appears red in reflected and blue in transmitted light, a colloidal solution of selenium and a black cathodic deposit of selenium being formed.

The internal friction of such colloidal selenium solutions is sensibly identical with that of the distilled water from which they are prepared, the same being the case with solutions prepared by Gutbier's method (Abstr., 1902, ii, 652). T. H. P.

Chemical Reactions in Gases Submitted to very High Pressures; Decomposition of Nitric Oxide; Formation of Nitrosyl Chloride. E. Briner and A. Wroczynski (*Compt. rend.*, 1909, **149**, 1372—1374. Compare Abstr., 1909, ii, 557).—Nitrosyl chloride is formed when a mixture of nitric oxide and hydrogen chloride is submitted to a pressure of 300 atmospheres. When nitric oxide is allowed to remain at high pressure in a sealed tube, it is colourless at first, but after a day appears bluish-green. If the tube contains a large quantity of the gas, drops of a blue liquid appear. The reaction is supposed to be represented by $6NO = 2N_2O_3 + N_2$; the synthesis of nitrosyl chloride would then be explained by the action $N_2O_3 + 2HCl = 2NOCl + H_2O$. No action occurs unless the nitric oxide is above a certain minimum pressure. In experiments in which the pressure in the tubes was gradually increased, the blue gaseous phase was first noticed at 28 atmospheres. The rate of formation of nitrosyl chloride increases with the pressure. W. O. W.

A New Chloride of Phosphorus. ADOLPHE BESSON and A. FOURNIER (*Compt. rend.*, 1910, **150**, 102—104).—On submitting a mixture of phosphorus trichloride and hydrogen to the action of an electric discharge (compare Abstr., 1909, ii, 663), a colourless liquid holding in suspension a yellow solid is produced. After filtration and purification by distillation under diminished pressure in an inert atmosphere, the liquid has a composition corresponding with that of phosphorus dichloride, P_2Cl_4. It is a colourless, oily, and strongly fuming liquid. The fuming is not only caused by the action of moisture, but also by oxidation, and under certain conditions the liquid takes fire spontaneously. It has b. p. about 180°/760 mm. (decomp.), 95—96°/20 mm. without decomposition, m. p. $-28°$. It is decomposed by water with the formation of phosphorous acid and a yellow solid of indefinite composition. It decomposes slowly at the ordinary temperature and more quickly when heated to phorphorus trichloride and a yellow to red solid of indefinite composition, which is possibly a mixture of amorphous phosphorus with other chlorides.

Attempts to prepare phosphorus dibromide in a similar manner, and also by the action of hydrobromic acid on the dichloride, were not successful. A yellow to red solid of indefinite composition was obtained, which, in the light of the results obtained with the dichloride, may have resulted from the decomposition of a dibromide. T. S. P.

Phosphorus Suboxide. ALFRED STOCK (*Chem. Zeit.*, 1909, **33**, 1354. Compare Burgess and Chapman, Trans., 1901, **79**, 1235).—Gutbier has stated (*Sitzungsber. physik.-med. Soc. Erlangen*, 1909, **40**, 176) that the existence of phosphorus suboxide (P_4O) may be considered as proved by the work of Weidner (*Inaug. Diss.*, Erlangen, 1909), who has repeated Michaelis and Pitsch's experiments (Abstr., 1900, ii, 137) and found, in agreement with them, that the substance in question does not contain hydrogen which is attached to phosphorus, any hydrogen present being due to moisture. The author points out that Michaelis and Pitsch's experiments are not conclusive, and that Weidner has adduced no fresh experimental evidence in support of the existence of phosphorus suboxide. T. S. P.

Formula of Hypophosphoric Acid. I. and II. E. CORNEC (*Bull. Soc. chim.*, 1909, [iv], **5**, 1081—1084, 1121—1126).—In the first paper the author reviews the evidence so far brought forward in favour of the simple, H_2PO_3, and double, $H_4P_2O_6$, formulæ for this acid. It is pointed out that the five sodium salts prepared by Salzer (Abstr., 1886, 420) can all be regarded as derived from an acid represented by the simple formula, and that evidence furnished by (1) the decomposition of the salts by heat (Salzer and Joly), and (2) the electrical conductivity (Rosenheim, Stadler, and Jacobson, Abstr., 1906, ii, 744, and by Parravano and Marini, *ibid.*, 744, 848) is not conclusively in favour of either, although the latter, by analogy with the case of sodium pyrophosphate, to a certain extent supports the double formula. Ebullioscopic determinations of the molecular weight of the methyl ester are in favour of the simple formula (Rosenheim, Stadler and Jacobson, *loc. cit.*).

In the second paper, the author gives the results of measurements of the lowering of freezing point of solutions of hypophosphoric acid, its potassium salts, and of solutions of the acid progressively neutralised with potassium hydroxide, sodium hydroxide, or ammonia (Abstr., 1909, ii, 972). These all afford evidence in favour of the double formula, $H_4P_2O_6$, for this acid (compare Parravano and Marini, *loc. cit.*). The only valid argument for the simple formula, H_2PO_3, still remaining is drawn from the esters of this acid, and these will now be further investigated. T. A. H.

Extinction of Flames. WILLEM P. JORISSEN and N. H. SIEWERTSZ VAN REESEMA (*Chem. Weekblad*, 1909, **6**, 1053—1062).—An investigation of the power of various gaseous mixtures to extinguish flame, and a review of previous work on this subject. A. J. W.

Inner Cone of the Bunsen Flame. FRITZ HABER and BURRITT S. LACY (*Zeitsch. physikal. Chem.*, 1909, **68**, 726—752).—The paper consists largely of a recapitulation and discussion of results already published by Haber's students and others (compare Haber and Richardt, Abstr., 1904, ii, 166; Davidson, Abstr., 1906, ii, 325; Tufts, *Physical Review*, 1906, **22**, 193; Lacy, Abstr., 1908, ii, 1033). The experiments of Davidson and of Tufts on the electrical conductivity of flames have been repeated by Lacy, but are only briefly described, as Epstein and Krassa have since made extended observations by an improved method; the results of which are shortly to be published.

All the observations indicate that, with a plentiful supply of air, the electrical conductivity of the inner green zone of the Bunsen flame is relatively high, and much exceeds that in the neighbouring non-luminous regions. Further, the velocity with which the water equilibrium is established is much less outside than inside the luminous zone. Reasons are advanced in favour of the view that these two phenomena are connected, both being due to the influence of gas ions in the green luminous zone. In this case the ions are produced as a consequence of the chemical changes taking place in the luminous zone. The effect of ionisation in accelerating the establishment of equilibria has already been investigated for the carbon monoxide flame by Haber and Coates (compare Abstr., 1909, ii, 997). G. S.

Nitrogen Compounds of Silicon. LUDWIG WEISS and THEODOR ENGELHARDT (*Zeitsch. anorg. Chem.*, 1909, **65**, 38—104).—A review of previous work on the ill-characterised silicon nitrides is given. Pure silicon is best prepared by reducing potassium silicofluoride with massive aluminium, a better regulus being obtained than when aluminium powder is used. The regulus is crushed and extracted successively with hydrochloric, concentrated sulphuric, and hydrofluoric acids. The product, even after repeated boiling in a state of fine powder with hydrofluoric acid, contains 0·3—0·5% Fe, 0·1% Cu, and 0·72% SiO_2. It forms brown, crystalline particles, D 2·30, and is not oxidised by oxygen at 700°.

Heated in pure nitrogen in a porcelain tube, combination begins near 1240°, the velocity of reaction increasing rapidly with the tempera-

ture. The product is amorphous and bulky, resembling cork, and is seen under the microscope to consist of several different substances. About 4% of the silicon volatilises, and forms a sublimate. The composition of the residue varies with the means of purification adopted. If boiled with potassium hydroxide solution, followed by hydrofluoric acid, a product having the formula Si_2N_3 is obtained, mixed with silica, which it is impossible to remove. If the free silicon is removed by boiling with a mixture of nitric and hydrofluoric acids, and the residue ignited and washed with hydrochloric acid, the compound SiN is obtained.

By heating silicon in nitrogen at 1300—1400° until saturated, a nitride of the approximate formula Si_3N_4 is formed, and is only slightly decomposed by treatment with potassium hydroxide and hydrofluoric acid, or with a mixture of nitric and hydrofluoric acids.

The *nitride* SiN is white, and has D 3·17; the nitride Si_2N_3 has D 3·64, and the nitride Si_3N_4, D 3·44, after allowing for the silica present. All the compounds are more or less decomposed by alkalis and by hydrofluoric acid.

Heating silicon in the flame of a coke fire gives a product containing carbon and nitrogen, corresponding approximately with the formula Si_3C_3N.

The estimation of nitrogen in the products is performed by heating with a mixture of equal parts of lead oxide, lead chromate, and lead peroxide in a porcelain tube in an atmosphere of carbon dioxide, increasing the temperature from 600 to 1000°. Kjeldahl's method gives less than half the total nitrogen. Silicon is estimated by fusion with potassium and sodium carbonates, as in the analysis of silicates. Commercial silicon is best analysed by fusion with potassium and sodium carbonates and potassium nitrate in a platinum crucible, which is first coated with a lining of the salt mixture before introducing the silicon. Any carborundum present is completely dissolved by these means. C. H. D.

Action of Metals on Fused Sodium Hydroxide. I. MAX LE BLANC and L. BERGMANN (*Ber.*, 1909, **42**, 4728—4747).—The action of various metals on fused sodium hydroxide at temperatures ranging between 400° and 720° has been investigated, all the experiments being carried out in an atmosphere of nitrogen. Preliminary experiments having shown that gold is the only metal which is not attacked by anhydrous, fused sodium hydroxide, the latter was always contained in a gold crucible, which was placed at the bottom of a silver tube surrounded by a porcelain tube. This tube could be heated to any desired temperature by an appropriate furnace arrangement. Pure dry nitrogen was passed through the reaction tube, and the extent of any reaction taking place was measured by determining the amount of water and hydrogen present in the issuing gas.

Sodium hydroxide can be readily dehydrated at a temperature of 400°, and undergoes no further loss in weight on heating to 720°, so that a dissociation corresponding with the equation: $2NaOH = Na_2O + H_2O$ does not take place between these temperatures.

Silver and sodium react with fused sodium hydroxide under

evolution of hydrogen; platinum, copper, iron, nickel, aluminium, zinc, and magnesium cause an evolution of hydrogen, and at the same time water is eliminated. The simplest explanation of this double reaction is that the compound $M(ONa)_x$, which is formed according to the equation: $M + xNaOH = M(ONa)_x + xH$, where M is a metal, forms a more or less complex compound with Na_2O, resulting from the loss of water from two molecules of the sodium hydroxide.

The valencies of the metals were calculated from the amount of hydrogen evolved, and found to be normal in the case of sodium, magnesium, copper, iron, aluminium, and zinc. Silver, nickel, and platinum gave abnormal values, as, for example, tervalent silver.

When the gold crucible containing sodium hydroxide and copper turnings was heated at 700°, it absorbed a not inconsiderable quantity of copper, forming an alloy. This alloy is not formed at this temperature in the absence of sodium hydroxide. When silver was used in place of copper, the silver became alloyed, and at the same time the silver tube containing the gold crucible took up some of the gold. The latter phenomenon was also noticed with nickel, but with none of the other metals. Magnesium also formed a gold-magnesium alloy.

T. S. P.

Alkali Hydrogen Carbonates. ROBERT DE FORCRAND (*Compt. rend.*, 1909, **149**, 825—829).—Hydrogen carbonates of the formula $R_2CO_3,2RHCO_3,xH_2O$, such as natural trona, have only occasionally been obtained in the laboratory. Dry potassium carbonate when left exposed to the air attains the composition $K_2CO_3,2KHCO_3$.

When dilute solutions of potassium, rubidium, and cæsium carbonates are exposed at room temperature for several weeks, carbon dioxide is absorbed until the composition corresponds with the formulæ: $8K_2CO_3,2KHCO_3$; $3Rb_2CO_3,2RbHCO_3$, and $4Cs_2CO_3,2CsHCO_3$. Although the amount of carbonic acid absorbed depends on the dilution, temperature, and pressure of carbon dioxide in the air, the results are held to indicate the formation of definite compounds. When solutions of hydrogen carbonates are boiled for prolonged periods, they are found to contain hydrogen carbonates of the same composition as the above, but the crystals deposited on evaporation have the composition: $5(K_2CO_3,1\frac{1}{2}H_2O),4KHCO_3$; $3(Rb_2CO_3,1\frac{1}{2}H_2O),2RbHCO_3$; $5(Cs_2CO_3,3\frac{1}{2}H_2O),2CsHCO_3$. The last is converted on the water-bath into $5(Cs_2CO_3,2H_2O),2CsHCO_3$.

The heats of formation of these hydrogen carbonates are negative and small in value.

R. J. C.

Hydrates of Rubidium and Cæsium Hydroxides. ROBERT DE FORCRAND (*Compt. rend.*, 1909, **149**, 1341—1344. Compare Abstr., 1906, ii, 445).—When an aqueous solution of rubidium hydroxide is allowed to evaporate at 15°, crystals of the hydrate $RbOH,2H_2O$ are deposited; these have m. p. 45—46°, and heat of solution $-0·646$ Cal. at 15°. The thermal properties of rubidium hydroxide and its hydrates are closely analogous with those of the corresponding potassium compounds.

The monohydrate of cæsium hydroxide already studied (*loc. cit.*) is more stable than those of the rubidium and potassium hydroxides. Although thermochemical measurements indicate the probable existence of a dihydrate, this has not yet been isolated, the crystals deposited when a solution of cæsium hydroxide is allowed to evaporate being those of the monohydrate contaminated by mother liquor.

A saturated solution of rubidium hydroxide at 15° contains 64·17% of RbOH, whilst a saturated solution of the cæsium compound contains 79·41% of CsOH. W. O. W.

Acid Sulphates. V. JOH. D'ANS (*Zeitsch. anorg. Chem.*, 1909, **65**, 228—230. Compare Abstr., 1909, ii, 885).—Determinations of the solubility of ammonium sulphate in mixtures of sulphuric acid and water at 25° indicate the separation of three solid phases: ammonium sulphate, and the acid salts $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4. The composition of the second salt was confirmed by isolation and titration. Washing with alcohol or ether is impracticable, on account of decomposition of the salt, and mechanical separation of the acid must therefore be employed.

Unlike sodium and potassium sulphates, the solubility of which increases with increasing sulphuric acid concentration, that of ammonium sulphate falls to a minimum, and then rises only very slightly to the limiting solution: $(NH_4)_2SO_4 - (NH_4)_3H(SO_4)_2$. The curve for $(NH_4)_3H(SO_4)_2$ also has a minimum. C. H. D.

Action of Heat and Light on Silver Sulphite and its Alkali Double Sulphites. Amount of Dithionate Obtained. HENRI BAUBIGNY (*Compt. rend.*, 1909, **149**, 858—860. Compare Abstr., 1909, ii, 1004).—Analysis of the products obtained by decomposing silver sulphite under various conditions shows that as much as 89·84% may be converted into dithionate, whilst the remainder is converted into sulphate. Sodium silver sulphite may give as much as 97·5% of sodium dithionate.

Silver sulphite is perfectly stable in the dark, but in diffused light it is slowly decomposed, giving dithionate and a small proportion of sulphate. R. J. C.

Necessity for Exactness in Describing Reactions. [Action of Heat on Sulphites.] HENRI BAUBIGNY (*Compt. rend.*, 1909, **149**, 1378).—Polemical against Colson (compare this vol., ii, 34), pointing out that nowhere in the literature is there the statement, ascribed by Colson to Berthier, that the double sulphites of the alkali metals and of silver decompose with the formation of sulphate. T. S. P.

New Preparation of the Second Anhydrous Modification of Calcium Sulphate. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1909, **65**, 105—107).—When either gypsum or the hemihydrate is dissolved in hot concentrated sulphuric acid, an anhydrous salt separates on cooling, which proves to be the second anhydrous calcium sulphate, known as Estrich gypsum. There are, in addition to the naturally occurring anhydrite, four anhydrous modifications of calcium sulphate.

(1) Kraut's anhydride, obtained at 100°; (2) van't Hoff's anhydride, also prepared at 100°, and hydrating very rapidly; (3) dead-burnt gypsum, prepared above 130°, incapable of hardening; (4) a modification prepared by heating above 530°, or by the action of sulphuric acid, hydrating very slowly. C. H. D.

Decomposition of Calcium Carbonate. ERNST H. RIESENFELD (*J. Chim. phys.*, 1909, **7**, 561—569).—New measurements of the dissociation pressure of calcium carbonate have been made with the object of explaining the discrepant results obtained by Brill (compare Abstr., 1905. ii, 522). The following values are recorded in mm. of mercury: 700°, 50; 750°, 99; 800°, 195; 850°, 370; 900°, 700. These data are in good agreement with the thermodynamic equation of Nernst, and by means of this equation the dissociation pressures are calculated for every 100° between 600° and 1500°. H. M. D.

Solubility of Cadmium Sulphide in Light Petroleum Containing Oil. G. C. A. VAN DORP and J. RODENBURG (*Chem. Weekblad*, 1909, **6**, 1038).—A colloidal solution of cadmium sulphide is obtained by triturating this substance with oil and adding light petroleum. A. J. W.

[Formation of Alloys by Pressure.] WALTHÈRE SPRING (*Zeitsch. Elektrochem.*, 1909, **15**, 984).—The author agrees with Tammann's view (Abstr., 1909, ii, 669) that the formation of alloys under pressure is a result of diffusion, which is not accelerated by the pressure. T. E.

Constitution and Heat Contents of Lead-Tin Alloys. W. GUERTLER (*Zeitsch. Elektrochem.*, 1909, **15**, 953—965).—The recent investigations of Rosenhain and Tucker (Abstr., 1908, ii, 1038) and of Degens (Abstr., 1909, ii, 888) leave the question of the cause of the development of heat at about 150° undecided; it may be due to decomposition of mixed crystals of lead and tin (Guertler, Abstr., 1909, ii, 319), or to the formation of a compound of about the composition Sn_3Pb_4. Using measurements of the quantity of heat given out by mixtures of lead and tin in cooling from 380° to 100° made by Spring in 1886, and the melting-point curve determined by Rosenhain and Tucker and Degens, the author has calculated the heats of fusion of different alloys of tin and lead. The values obtained are very much larger than those calculated on the assumption that the heat of fusion of the alloy is the mean of the heats of fusion of its constituents. This shows that liquid tin and lead must give out a considerable quantity of heat when they are mixed together. T. E.

Peroxidised Compounds. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1909, **65**, 25—31).—The isolation of a salt, $Pb_2Se_2O_7$ (Abstr., 1909, ii, 575), proved lead sesquioxide to be a true feebly-basic oxide, and not a salt of the dioxide. In the attempt to prepare other sesquioxides, the liquid obtained by the addition of an acid solution

of potassium permanganate to a mixture of hydrogen peroxide and sulphuric acid at $-15°$, supposed by Berthelot to contain the compound H_2O_3, has been examined.

The solution is capable of oxidising sulphurous acid completely to sulphuric acid. It is probable that the compound present is a higher acid of manganese, as the curve connecting volume of oxygen evolved, in the absence of sulphurous acid, with time has exactly the same form as that obtained with a mixture of chromic acid and hydrogen peroxide, in which perchromic acid is known to be present. It is shown that the oxidation of the sulphurous acid is not due to the action of free oxygen in supersaturated solution. C. H. D.

Relation of Thallium to the Alkali Metals: a Study of Thallium Zinc Sulphate and Selenate. ALFRED E. H. TUTTON (*Proc. Roy. Soc.*, 1910, **83**, *A*, 211—226).—A detailed crystallographic examination of the double salts: $Tl_2SO_4,ZnSO_4,6H_2O$ and $Tl_2SeO_4,ZnSeO_4,6H_2O$ has been made.

The various crystallographic data and the morphological angles are tabulated. The double sulphate was found to have D 3·7204 by the author's pyknometer method; consistent results could not be obtained for the double selenate.

From a comparison of the thallium salts with the corresponding potassium, rubidium, ammonium, and cæsium salts, the author concludes that the morphological and physical properties of the crystals of the thallium double salts are such as quite entitle them to places in this isomorphous series, but not to places in the more exclusive eutropic series obeying the law of progression according to the atomic weight of the interchangeable metals.

The position of thallium in either the simple or double salt series is very close to that of ammonium, and therefore also to that of rubidium. This does not hold, however, for the refractive power. In respect of this property, the thallium double salts are quite exceptional, in that they exhibit abnormally high refraction, and a larger amount of dispersion and of double refraction. The mean refractive index of thallium zinc sulphate for sodium light is 1·6064, whereas the values for the other four double sulphates range from 1·4859 to 1·5054. H. M. D.

Acid Sulphates. VI. JOH. D'ANS and O. FRITSCHE (*Zeitsch. anorg. Chem.*, 1909, **65**, 231—232. Compare this vol., ii, 125).—Thallium sulphate and dilute sulphuric acid form two acid salts, $Tl_3H(SO_4)_2$ and $TlHSO_4$, the limits of existence of which at 25° have been determined. The curves differ from those of the alkali sulphates, the solubility increasing almost continuously with the sulphuric acid concentration. C. H. D.

The System Mercuric Chloride and Mercurous Chloride. W. P. A. JONKER (*Chem. Weekblad*, 1909, **6**, 1035—1038).—Mercuric chloride has m. p. 277° and b. p. 301°. Addition of mercurous chloride lowers the m. p. to the eutectic point 271°. A saturated solution of mercurous chloride in mercuric chloride contains 12% of the former, and has b. p. 304°. Mercurous chloride sublimes at 373°. A. J. W.

Resolution of Ytterbium. CARL AUER VON WELSBACH (*Monatsh.*, 1909, **30**, 695—700+i—vi).—Polemical (compare Welsbach, Abstr., 1908, ii, 591). Disputes Urbain's claim of priority (compare Abstr., 1907, ii, 956; 1908, ii, 849). E. F. A.

Electrical Properties of Aluminium Copper Alloys. WITOLD BRONIEWSKI (*Compt. rend.*, 1909, **149**, 853—855. Compare Pushin, Abstr., 1907, ii, 774).—Determinations were made of the electrical conductivity, temperature-coefficient of resistance, solution potential, and thermoelectric power of a complete series of alloys of copper and aluminium. Alloys containing more than 12% of either metal, which are very brittle, had not been investigated previously. The electrical properties in question were often greatly modified by annealing, but the inferences drawn from the curves of both tempered and annealed alloys are the same. The annealing was carried out in an electric furnace for four to five hours at a temperature somewhat below the solidus of each alloy.

The curves indicate the compounds Al_2Cu, $AlCu$, Al_2Cu_3, $AlCu_3$. The compound Al_2Cu_3 has not been detected previously, but the other three were found by Le Chatelier and by Guillet (Abstr., 1905, ii, 712). Carpenter and Edwards (1907) found no evidence for the compound $AlCu$, but, on the other hand, their compound $AlCu_4$ could not be detected by the author.

The compound $AlCu_2$ is depolymerised above 500°, when the larger crystals are split up into finely crystalline masses, and the electrical resistance is doubled. R. J. C.

Crystalline Structure of Iron at High Temperatures. WALTER ROSENHAIN and J. C. W. HUMFREY (*Proc. Roy. Soc.*, 1910, **83**, *A*, 200—209).—The structural changes which accompany the deformation of iron at high temperatures have been investigated. The material employed for most of the experiments was a pure form of commercial iron of very low carbon content. To remove oxygen, the metal was heated to about 900° in a current of pure dry hydrogen. A strip of this iron, the surface of which had been polished previously, was then placed in a specially designed piece of apparatus, in which it could be electrically heated in a vacuum and subjected to stress whilst at a high temperature. By means of comparative observations on specimens which were heated without straining, the changes in the structure which resulted from the rise of temperature could be distinguished from those which were a consequence of the applied stress.

Under the conditions of the experiments, the strips of metal were not uniformly heated, and whereas the temperature of the central portion exceeded 1000°, the metal at and near the ends did not reach a visible red heat. Corresponding with the distribution of temperature, the micro-structure exhibits three distinct regions when the strips are examined from the central portion towards either end.

The structural differences lead to the conclusion that pure iron between the ordinary temperature and 1000° exists in three distinct modifications possessing widely different mechanical properties. The temperature ranges in which these modifications exist are consistent with

the view that they are identical with the α-, β-, and γ-forms of Osmond and Roberts-Austen, as indicated by cooling curves. The deformation observations also indicate that β-iron, although existing at a higher temperature, is harder and stronger than α-iron, and that the reversible transformation of these forms is accompanied by a change of volume. The γ-iron obtained in the case of approximately pure iron exhibits the structure and properties of the "γ-iron" alloy steels.

H. M. D.

Passivity of Iron. P. KRASSA (*Zeitsch. Elektrochem.*, 1909, **15**, 981—984).—A reply to Müller and Königsberger (Abstr., 1909, ii, 1016). The author maintains his former criticism (Abstr., 1909, ii, 738), and insists further that the potentials of Müller and Königsberger's mirrors were so abnormal that their behaviour cannot be regarded as proving anything about ordinary iron. T. E.

Retardation of the Oxidation of Iron by Chromic Chloride. PAUL ROHLAND (*Zeitsch. Elektrochem.*, 1905, **15**, 865—866).—Chromic chloride retards the oxidation of iron; an increase of the concentration of the hydrogen ions in the solution causes the protection to disappear. The action persists in presence of chlorine ions, and to a less extent in presence of bromine ions. Ferric chloride is, however, an exception; possibly the hydrogen ions formed by hydrolysis account for this. Chromic ions protect iron in presence of sulphates, but not in presence of nitrates. T. E.

Carbon Monoxide in Steels. E. GOUTAL (*Compt. rend.*, 1909, **149**, 1129—1131).—The author has shown previously (Abstr., 1909, ii, 519) that when steels are dissolved in solutions of copper salts, gases are evolved which contain carbon dioxide and monoxide. The percentage of carbon monoxide was estimated by making use of the oxidising action of iodine pentoxide at 75°, and found to have a mean value of 0·014%. These results are now confirmed as follows. The evolved gases were swept by a current of nitrogen through a series of tubes, each containing 25 c.c. of a 1% solution of defibrinated guinea-pig's blood. Each tube could absorb a known quantity of carbon monoxide, and by determining the number of tubes which showed the characteristic absorption spectrum of carbon monoxide-hæmoglobin, the percentage of carbon monoxide could be found.

The percentages thus determined are independent of: (1) the amount of steel taken; (2) the duration of the experiment; (3) the acidity of the copper solution used; (4) the substitution of cupric chloride by a solution of iodine in potassium iodide; (5) the gas (air or nitrogen) employed for sweeping out the evolved gases.

Analyses of different steels show that the percentage of carbon monoxide does not appreciably exceed 0·014. This percentage (0·014) remains approximately constant for ordinary steels containing more than 0·3% of carbon. Nickel steels contain a much less, and chromium steels about the same, percentage of carbon monoxide as ordinary steels of the same carbon content.

Samples of steel were taken from a Siemens Martin furnace one

hour and then forty-five minutes before tapping, and also just before and just after the addition of ferro-manganese. The percentage of carbon monoxide remains practically constant during the period of decarburisation; it then falls considerably just before the addition of ferro-manganese, to rise to its final value after the ferro-manganese has been added. This is true for both soft and hard steels, in which the percentages of carbon monoxide are respectively 0·0063 and 0·0137. T. S. P.

Oxygen Evolved from Ferric Oxide at High Temperatures. SIEGFRIED HILPERT (*Ber.*, 1909, **42**, 4893—4895).—In contradistinction to Walden (Abstr., 1908, ii, 852), the author has not been able to determine the temperature at which the pressure of oxygen over ferric oxide is equal to that of the atmosphere. The results vary considerably with the method of preparation and previous treatment of the ferric oxide, and the velocity with which equilibrium is attained is extremely slow. In general, the amount of ferrous oxide formed by heating ferric oxide in the air to 1300° did not exceed 5°; only above 1350° was there further loss of oxygen. In one experiment, heating the ferric oxide to 1600° only increased the percentage of ferrous oxide from 2·95 to 3·1%.

It is pointed out that thermodynamical calculations according to Nernst's theorem are totally untrustworthy when the dissociation of such substances as ferric oxide is taken as the basis. T. S. P.

Phosphorus Compounds of Iron. N. S. KONSTANINOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1220—1240).—The alloys of phosphorus and iron were divided by Stead (*J. Iron and Steel Inst.*, 1900, **58**, 60) into five classes: (1) those containing 0—1·7% of phosphorus and consisting of solid solutions of Fe_3P in iron; (2) alloys with 1·7—10·2% of phosphorus, which form solid solutions of Fe_3P in iron and give a eutectic alloy (10·2% P) consisting of a definite solid solution and the phosphide Fe_3P; (3) those with 10·2—15·58% P, also consisting of the eutectic and Fe_3P, the m. p. of the latter (15·58% P) being 1060°; (4) alloys containing 15·58—21·6% P and consisting of Fe_3P and Fe_2P; (5) those with more than 21·6% P and containing Fe_2P and another phosphide richer in phosphorus. These results were confirmed by Saklatwalla (*J. Iron and Steel Inst.*, 1908, **77**, 92—103), who gave a melting-point diagram for these alloys.

The author's investigations of iron-phosphorus alloys containing up to 21·0% (32·4 atom.%) of phosphorus show that the solidification-point diagram consists of three branches: (1) *AB*, falling from 1514°, the m. p. of iron, to 1020°, corresponding with 10·2% Fe; (2) *BC*, rising continuously from *B* to *C*, and corresponding with the separation of crystals of the phosphide Fe_3P. The separate solidification curves exhibit two halts, one showing a regular rise corresponding with the separation of crystals of the phosphide, and the other at a constant temperature corresponding with separation of the eutectic and gradually diminishing in magnitude as *C* is approached. Micrographic examination of these alloys shows the presence of rhomboidal plates of Fe_3P surrounded by the eutectic; (3) *CD*, rising at first rapidly and

afterwards more slowly to the point *D*, corresponding with the phosphide Fe_2P (compare Gercke, Abstr., 1908, ii, 1041; Le Chatelier and Wologdine, Abstr., 1909, ii, 1017).

A list is given of the known phosphides, arsenides, and antimonides of the metals of the iron series of the eighth group in the periodic system. With the typical metals of this series, iron, cobalt, and nickel, these compounds are more varied in type than with the initial members, manganese and copper. With the metals of the other groups of the periodic system, these compounds are, in the great majority of cases, derived from the hydrogen phosphides PH_3 and PH_2. With phosphorus, the most stable compounds are those rich in metal, such as M_3P, whilst with arsenic and especially with antimony, compounds relatively poor in metal, such as MSb_2, are the most stable.

T. H. P.

Iron Phosphides. OTTO KUHN (*Chem. Zeit.*, 1910, **34**, 45—46).—Le Chatelier and Wologdine (Abstr., 1909, ii, 1017) state that there are only four iron phosphides, namely, Fe_3P, Fe_2P, FeP, and Fe_2P_3, and, further, that the existence of the last two has not been proved with absolute certainty. In the course of an investigation on the preparation of copper phosphide by heating a mixture of bone ash, powdered quartz, wood-charcoal, and granulated copper, the author obtained a product which, on solution in nitric acid, left a small residue of glistening needles, which were practically insoluble in hot or cold concentrated nitric acid or in dilute sulphuric acid, although readily soluble in aqua regia. The results of analysis agree approximately with the formula Fe_5P_2, the iron coming from the impure quartz used in the preparation. These needles cannot be considered as a solid solution of Fe_3P and Fe_2P, since the former compound is readily soluble in nitric acid. T. S. P.

Electromotive Forces of Cobalt Alloys. F. DUCELLIEZ (*Compt. rend.*, 1910, **150**, 98—101. Compare Pushin, Abstr., 1907, ii, 325, 618, 774, 837).—From the curves showing the relation between the composition of the alloy and the potential with respect to a normal solution of cobalt sulphate, the existence of the following compounds has been deduced: CoSn, CoSb, $CoSb_2$. Alloys of cobalt and bismuth form two phases, the one rich in cobalt, and the other and heavier, rich in bismuth. Bismuth lowers the melting point of the cobalt which, when liquid, is capable of dissolving some bismuth. From liquid alloys containing 0—94 (approx.) % Bi, the cobalt separates in a pure state on cooling. The results obtained with lead and cobalt are similar to those with bismuth and cobalt. Cobalt and copper do not form compounds with each other, but give either homogeneous solid solutions or two phase systems of solid solutions. T. S. P.

Absorption of Carbon by Metals, Especially Nickel, in the Electrolysis of Aqueous Solutions. GUSTAV LAMBRIS (*Zeitsch. Elektrochem.*, 1909, **15**, 973—981).—The nickel which is deposited from a solution containing ammonium oxalate contains up to 4% of carbon; the smaller the quantity of nickel deposited and the larger

the quantity of ammonium oxalate used, the greater is the quantity of carbon in the deposit. The carbonaceous residue obtained by dissolving the nickel by copper chloride and chlorine contained ammonium chloride, which could not be completely removed. The percentage of carbon in the residue increased as greater precautions were taken to free it from ammonium salts. The ammonium salts of glycollic, formic, and acetic acids also yield nickel containing carbon, but if a diaphragm is interposed between the anode and cathode, carbon-free nickel is obtained if the cathode solution contains free ammonia, but not if it is kept slightly acid. Carbon dioxide also gives carbonaceous nickel (from nickel ammonium sulphate solution), but in presence of a little free ammonia, carbon-free metal is obtained. Since the metal obtained from ammonium oxalate solution contains carbon even in presence of a large excess of free ammonia, the anodic carbon dioxide cannot be the source of the carbon. The same applies to carbon monoxide, which behaves in the same way as carbon dioxide. Methane, ethane, and ethylene give carbon-free nickel, but acetylene, passed into the cathode solution, gives carbonaceous nickel both in neutral and strongly ammoniacal solutions.

It is shown that acetylene is formed in small quantities at the cathode when ammonium oxalate is electrolysed with platinum and nickel cathodes, but not with iron, copper, or tin; some ethane is also formed by further reduction of the acetylene.

The carbon is contained in the nickel in the form of a carbide; when the metal is dissolved in hydrochloric acid, the whole of the carbon is evolved in the form of hydrocarbons.

Iron, at which no acetylene is formed, is deposited from ammonium oxalate solutions quite free from carbon. It appears, therefore, quite clear that the carbon is contained in the nickel as carbide, formed from acetylene during the deposition of the nickel. T. E.

Alloys of Nickel and Copper. ÉMILE VIGOUROUX (*Compt. rend.*, 1909, **149**, 1378—1380. Compare Kurnakoff, Abstr., 1907, ii, 525; Guertler, Abstr., 1908, ii, 557).—From an examination of the action of acids on alloys of copper and nickel, and by determinations of the *E.M.F.* produced in cells when one of the metals constitutes one of the electrodes and an alloy of the two the second electrode, the author is led to the conclusion that no definite compounds of nickel and copper exist. W. O. W.

Two New Nickel Phosphides. PIERRE JOLIBOIS (*Compt. rend.*, 1910, **150**, 106—108).—Twenty-one grams of an alloy of tin and nickel containing 5% of nickel were heated with 1—4 grams of phosphorus in a vacuous sealed tube to 700°. On cooling and dissolving the lower part of the ingot obtained in warm concentrated hydrochloric acid, small, prismatic crystals of metallic appearance were left, having a composition corresponding with the formula NiP_2, and $D^{18} = 4{\cdot}62$. They are soluble in nitric acid, decomposed by fused sodium hydroxide, and lose their phosphorus at 650°.

If the proportion of phosphorus in the reaction mixture is increased to 7—10 grams, hydrochloric acid leaves a mixture of tin phosphide

(SnP_3) with another nickel phosphide, having the formula NiP_3. These are separated by heating the mixture in a vacuum to 360°, whereby the compound SnP_3 loses phosphorus, giving the compound Sn_4P_3 (compare Abstr., 1909, ii, 319), which is then readily soluble in hydrochloric acid. This second phosphide of nickel forms microscopic crystals of metallic appearance, which are readily soluble in nitric acid, and is decomposed, with incandescence, by fused sodium hydroxide; the phosphorus is lost at 580°; $D^{18} = 4{\cdot}19$.

T. S. P.

Mixed Halogen Compounds of Tin. VICTOR AUGER (*Compt. rend.*, 1909, **149**, 860—862).—Numerous compounds of the types: $SnCl_3Br$, $SnCl_2Br_2$, $SnClBr_3$ have been described, all of which are said to decompose on distillation into the simple stannic salts: SnX_4, SnY_4.

The author shows that mixtures of $SnBr_4$ and SnI_4 give a normal freezing-point curve with a eutectic at the composition $SnBr_{3\cdot2}I_{0\cdot8}$. The supposed compound, $SnBr_2I_2$, melting at 54° is identical with an equimolecular mixture of $SnBr_4$ and SnI_4, and may be separated by a series of ten fractional crystallisations into fractions melting at 88° and 27°, of compositions $SnBr_{1\cdot2}I_{2\cdot8}$ and $SnBr_{2\cdot7}I_{1\cdot3}$ respectively. Similarly, the supposed compounds $SnBrI_3$ (m. p. 103°) and $SnBr_3I$ may be partly resolved by crystallisation.

The cooling curve of $SnBr_2I_2$ from 55° is an unbroken line, such as is given by a mixture, although the crystals are brilliant and apparently homogeneous. The author suggests that in all molten mixtures of the composition $SnBr_aI_{(4-a)}$, the halogen atoms are perfectly mobile. The same is suggested for the chlorobromides and iodochlorides.

R. J. C.

Natural Zirconium Dioxide. LUDWIG WEISS [and, in part, RICHARD LEHMANN] (*Zeitsch. anorg. Chem.*, 1909, **65**, 178—227).—Native zirconium dioxide, baddeleyite, instead of being isomorphous with rutile and cassiterite, is monoclinic. If artificially crystallised from borax, however, it is quadratic, and isomorphous with rutile. Several hundred kilograms of the native mineral from Brazil have been used for the investigation. It contains 88·09% ZrO_2, 7·39% SiO_2, 0·74% TiO_2, and 3·78% Fe_2O_3. About one-half of the impurities may be removed by boiling with hydrochloric acid, and rather more by heating with sodium sulphate, salt, and carbon. Pure zirconia is obtained by heating the mineral with potassium hydrogen fluoride, and crystallising the double fluoride.

For analysis, the mineral is fused with sodium hydrogen sulphate. Iron is separated, with aluminium if present in small quantity, by precipitation with ammonium sulphide from a hot solution containing ammonium oxalate and tartrate. After removal of organic salts from the filtrate, the zirconium hydroxide is precipitated with sodium hydroxide and hydrogen peroxide, titanium being left in solution. The following analyses represent dense fragments:

	ZrO_2.	Fe_2O_3.	Al_2O_3.	TiO_2.	SiO_2.	H_2O.	Total.
I.	92·07	2·73	1·17	trace	2·73	0·88	99·58
II.	84·96	7·01	3·99	trace	1·57	1·04	98·57

Pure zirconia is obtained by a long process, which is described in detail. Repeated fractionation does not produce any indication of a separation of the zirconium into two constituents. Small quantities of rare earths have been recognised spectroscopically, but scandium is present only in faint traces.

The specific gravity varies, even of pure samples, and is apparently dependent on the extent of the previous heating. After compressing to form rods under a pressure of 8000 kilograms per sq. cm., it may be fused by a powerful arc, using 500 amperes or more, and then has $D^{18.5°}$ 5·48. The linear coefficient of expansion is $\alpha = 0.00000084$, very near to that of fused quartz. Crucibles, etc., may be made by mixing the zirconia with 10% of magnesia, or clay. Platinum may be rendered completely liquid by heating in a zirconia crucible with an oxy-hydrogen flame. Quartz may also be melted without destruction of the crucible. Other technical applications are described.

C. H. D.

Thorium. H. von Wartenberg (*Zeitsch. Elektrochem.*, 1909, **15**, 866—872).—Thorium is prepared by electrolysis of thorium chloride dissolved in a mixture of fused potassium and sodium chlorides (Abstr., 1906, ii, 678). The action of the electrolyte on the porcelain crucible is avoided to a great extent by using a graphite crucible which fits closely into the porcelain crucible, both as anode and as containing vessel for the fused salts. The cathode is a graphite rod, and the electrolysis is carried out as rapidly as possible in an atmosphere of nitrogen. The metal is obtained in the form of crystals mixed with carbon, from which it is separated by means of methylene iodide. Careful analyses gave 87·6 to 88·9% thorium, 0·06% iron, 0·04% sodium, 0·03% silicon, and 0·15% carbon (mechanically admixed). The remainder was oxide. Microscopic examination showed this to be mixed with the metal; it is left in the form of a felted mass when the metal is dissolved in acid. Experiments with mixtures of lead and thallium with their oxides show that mechanically-admixed oxides do not affect the ductility of these soft metals very seriously, so that the ductility of thorium cannot be used as an argument in favour of its purity (Abstr., 1909, ii, 53). The heats of formation of thorium oxide and chloride were determined and corrected for the impurities present:

$$Th + O_2 = ThO_2 + 326.0 \pm 0.5\% \text{ Cal.}$$

$$Th + 2Cl_2 = ThCl_4 + 300.2 \pm 0.67\% \text{ Cal.}$$

The results are given in kilogram calories.

The metal melted at 1700°, but the carbon in it combined with it, forming about 2% of carbide, which would lower the melting point very considerably. Thorium sulphide has been prepared, and its formula is shown to be ThS_2.

T. E.

The Atomic Weight of Vanadium. Wilhelm Prandtl and Benno Bleyer (*Zeitsch. anorg. Chem.*, 1909, **65**, 152—165).—Vanadium oxy-trichloride, $VOCl_3$, is the only vanadium compound capable of being obtained in a state of sufficient purity for atomic weight determinations. Ammonium metavanadate is three times precipitated from its boiling solution with ammonium chloride, ignited,

heated with hydrofluoric acid, and then mixed with carbon and ignited, first in a current of hydrogen and then in one of chlorine. The product is fractionally distilled, and then has b. p. 124·4°/723 mm. (corr.). When no longer changed by further fractionation, it has $D_4^{15\cdot5}$ 1·8362. The vapour density proves it to be undecomposed.

The liquid is distilled into glass bulbs and weighed; the bulbs are broken in glass flasks containing water and zinc. After acidifying with nitric acid and filtering, the chlorine is precipitated with silver nitrate. The mean result of nine determinations obtained is V = 51·0 (Ag = 107·880; Cl = 35·460), which is lower than the previously accepted value, 51·2. The difference is explained by a criticism of Roscoe's method. C. H. D.

Solution of Platinum in Sulphuric Acid and the Products of Reaction. MARCEL DELÉPINE (*Compt. rend.*, 1910, **150**, 104—106).—Quennessen (Abstr., 1906, ii, 551) has attributed the solvent action of sulphuric acid on platinum to the intermediate action of oxygen of the air. The author shows that all Quennessen's results can be explained by assuming that the reaction, as represented by the equation $2Pt + 7H_2SO_4 \rightleftharpoons 2OH{\cdot}Pt(SO_4H)_2 + 3SO_2 + 4H_2O$, is reversible. Sulphuric acid and spongy platinum were boiled up together in a flask, while various gases were passed through the liquid. With carbon dioxide, the reaction proceeded according to the above equation. When air was used, twice as much platinum dissolved, and less sulphur dioxide was evolved, owing to the oxidation of the sulphur dioxide to trioxide under the influence of the platinum. With oxygen, four times as much platinum dissolved, and less still sulphur dioxide was evolved. When a mixture of carbon and sulphur dioxides was used, no solution of platinum took place, and, in some cases, platinum was precipitated from solution.

The compound of platinum mentioned above can be isolated in the form of the potassium salt, $OH{\cdot}Pt(SO_4H){\cdot}SO_4K$, by adding a dilute solution of a potassium salt to the orange-yellow liquid. If the platinum is boiled with sulphuric acid for a long time, the liquid becomes darker and darker in colour, finally almost black, and after thirty hours may contain more than 20 grams of platinum per litre. From this solution a brown compound can be obtained, having the formula $Pt(OH)_2{\cdot}SO_4H,H_2O$, and crystallising in rectangular prisms, which are very soluble in water, concentrated sulphuric acid, alcohol and acetone. At 100° it loses $1{\cdot}5H_2O$. The compounds can also be obtained by the oxidation of platinum dioxide with nitric acid.

T. S. P.

Mineralogical Chemistry.

Volcanic Gases. ALBERT BRUN (*Bull. Soc. chim.*, 1910, [iv], 7, 4). —It is pointed out that the use of the word "fumarole" in Gautier's re-statement (*Bull. Soc. chim.*, 1909, [iv], 5, 982; compare Abstr.,

1909, ii, 744, 745) of the author's argument in favour of the view that aqueous vapour is of little importance in volcanic explosions (Abstr., 1907, ii, 33), is confusing. T. A. H.

Gas from Thermal Springs: Presence of Krypton and Xenon. CHARLES MOUREU and A. LEPAPE (*Compt. rend.*, 1909, **149**, 1171—1174).—The authors have recognised the presence of krypton and xenon in twenty-six French thermal springs. The fact was established that the gases did not come from the atmosphere in the vicinity of the springs. W. O. W.

Dawsonite, a Sodium-Aluminium Carbonate. RICHARD P. D. GRAHAM (*Trans. Roy. Soc. Canada*, [iii], **2**, iv, 165—177).—This mineral is found in two dykes in Montreal, at Ténes, Algeria, and in Tuscany. Terminated crystals are very rare, but the author found a few belonging to the orthorhombic, holosymmetric class [$a:b:c=$ 0·6475 : 1 : 0·5339]. The optical properties were studied. Some very pure crystals on analysis gave

Al_2O_3.	Na_2O.	CaO.	MgO.	CO_2.	H_2O.
35·70	21·62	1·59	trace	31·56	11·51

agreeing with the formula $Al_2O_3,Na_2O,2CO_2,2H_2O$. A small amount of calcium was present as admixed calcite. Neither water nor carbon dioxide is lost at 140°; long heating at high temperature is necessary to expel these constituents completely. Two constitutional formulæ are suggested: ONa·Al(OH)·O·CO·OH and $Al(OH)_2$·O·CO·ONa, the first of which is considered the more probable. E. J. R.

Chemical Investigation of a Uranium Mineral from Borneo. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1909, [vi], **3**, 1203—1212).—This mineral occurs in well-formed, iron-black crystals, D^{16} 9·057, hardness 5—6, exhibiting marked radioactive properties. The analytical results of two different specimens are as follows:

SiO_2.	UO_3.	UO_2.	PbO.	ThO_2.	Y_2O_3, etc.	CaO.	FeO.
0·77	40·95	41·24	8·51	5·03	1·56	0·18	0·91
0·76	40·38	41 15	8·49	5·00	1·57	0·18	0·90

Bi_2O_3.	MgO.	CuO.	H_2O.	Total.	D^{16}.
trace	trace	—	0·52	99·67	9·059
—	trace	trace	0·52	99·45	9·056

These numbers show that the mineral consists of bröggerite, the corresponding formula being:

$$4SiO_2,45UO_3,48UO_2,12PbO,6ThO_2,2Y_2O_3,CaO,4FeO,9H_2O.$$

Further analysis of the rare earth constituent shows that it contains ytterbia and ceria in the proportion $Y_2O_3 : Ce_2O_3 = 5 : 1$, the ceria fraction containing oxides of cerium, lanthanum, neodymium, and praseodymium in the proportions: $Ce_2O_3 : La_2O_3 : Nd_2O_3 : Pr_2O_3 =$ 8 : 5 : 1 : 2. T. H. P.

Isomerism in the Group of Alumino- and Ferri-silicates. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1909, [vi], **3**, 1183—1202).—In addition to alumino-(or ferri-)silicates having the

structure of kaolinite (derivatives of clay), chloritoids (derivatives of $M_2Al_2SiO_6$), and chlorites [derivatives of $Al_2Si_{2+m}O_{8+2m-n}(OH)_{2n}$ or $Al_2SiO_{5-n}(OH)_{2n}$], a group of alumino-silicates is possibly derived from orthosilicates, and having the general formula : $(M_2SiO_4)_p,qA$, where $A = MAl_2Si_2O_8$ (or $MFe_2Si_2O_8$) or MAl_2SiO_6. To this group belong: (1) melilite, $(Ca_2SiO_4)_p,qCaAl_2Si_2O_8$, where $p = 3{\cdot}5$ and $q = 1{\cdot}2$; (2) gehlenite, $Ca_2SiO_4CaAl_2SiO_6$, and (3) ilvaite, $H_2O-(Fe_2SiO_4)_p-CaFe_2Si_2O_8$, where $p = 2$. In their properties these compounds differ from the compounds $MAl_2Si_2O_8$, and approximate to the minerals M_2SiO_4. This series of silicates is analogous to the kaolinite series and to the granites isomeric with them.

Isomerism in the kaolinite series is of three kinds: (1) symmetry isomerism; (2) transposition isomerism, an example of which is shown by the granite, $CaAl_2Si_2O_8$(nucleus),Ca_2SiO_4, and the member of the melilite series, Ca_2SiO_4(nucleus),$CaAl_2Si_2O_8$; (3) isomerism of rearrangement, as seen in lawsonite, $CaAl_2Si_2O_8,2H_2O$, and Gibbsite, $H_2Al_2Si_2O_8,CaO,H_2O$. T. H. P.

Physiological Chemistry.

Acapnia and Shock. IV. Fatal Apnœa after Excessive Respiration. YANDELL HENDERSON (*Amer. J. Physiol.*, 1910, **25**, 310—333. Compare Abstr., 1909, ii, 421).—One of the most marked symptoms of pain is hyperpnœa, and the drugs which relieve pain quiet breathing. The forced breathing leads to apnœa, owing to the carbon dioxide being swept out of the body; the apnœa in the end leads to the phenomena of shock; and, in fact, the symptoms of shock can be induced in normal men and animals by excessive ventilation of the lungs. This in animals can be carried so far as to be fatal. This is due to lack of oxygen, primarily produced by the inactivity of the respiratory centre, which is not excited owing to the absence of carbon dioxide. The administration of that gas during apnœa causes breathing to recommence. Failure of respiration after intense pain is produced in the same way. W. D. H.

Union of Oxygen in Blood. WILHELM MANCHOT [and, in part, W. BRANDT] (*Annalen*, 1909, **370**, 241—285).—An investigation on the relationship existing between the absorption of certain gases by blood and (1) the temperature, (2) the partial pressure of the gas, and (3) the concentration of the blood, carried out with the object of obtaining information on the absorption of oxygen by blood.

A complete analogy is found to exist between the metallic salts which combine with gases, and blood-pigment in their behaviour towards certain gases; thus, not only does blood-pigment combine with acetylene, carbon monoxide, ethylene, nitric oxide, and oxygen, but the dissociation is conditioned by the same factors as those which determine

the dissociation of the compounds of cuprous chloride with these gases (compare Manchot and Friend, Abstr., 1908, ii, 375 Manchot and Brandt, this vol., i, 85).

The compounds of hæmoglobin with acetylene and ethylene are dissociated to the greatest extent, whilst the degree of dissociation of the oxygen compound is slightly greater than that of the compound with carbon monoxide or nitric oxide. Changes of temperature and pressure produce a greater effect on the ethylene compound than on the carbon monoxide compound; in the case of the former substance, the effect produced by altering the temperature is due rather to an alteration in the state of equilibrium than to the change in the concentration of the gas.

Blood which has been reduced by means of hydrogen, likewise natural blood, when diluted with water, serum, or isotonic solutions of sodium chloride or sucrose, combines with a greater proportion of oxygen, carbon monoxide, ethylene, or nitric oxide than undiluted blood. The same observation was made with the blood of horses, oxen, and pigs. The absorption reaches a maximum at a dilution of about eight to ten times, at which point each atomic proportion of iron is found to combine with practically two molecular proportions of the gas. The effect of further dilution, likewise the addition of alkali, is to decrease the absorption of gas, owing to the hydrolysis of the additive compound.

Since the gases, oxygen, carbon monoxide, nitric oxide, ethylene, and probably also acetylene, are absorbed in equimolecular proportions, it follows that the absorption of these gases by hæmoglobin is not brought about through the agency of individual valencies, but through the mutual attraction of the molecules as a whole with the formation of a molecular complex, as in the case of the union of cuprous chloride and carbon monoxide (*loc. cit.*).

Blood which has been acted on by hydrogen for some time after the complete reduction of the oxyhæmoglobin is found to absorb more oxygen than that which has not been thus treated; this is shown to be due to the presence of carbon dioxide, which is slowly removed by the hydrogen. Carbon dioxide in this respect behaves like hydrogen chloride with carbon monoxide and cuprous chloride (*loc. cit.*).

The latter part of the paper is devoted to a discussion of the absorption of oxygen by the blood in respiration, and the effect of carbon dioxide on the tension of the oxygen in blood. It is shown that the presence of uncombined hæmoglobin in the blood (natural blood contains roughly one molecular proportion of oxygen per atomic proportion of iron) tends to keep the velocity of absorption of oxygen under different pressures constant. W. H. G.

Physiology of Water and Sodium Chloride. OTTO COHNHEIM, KREGLINGER and KREGLINGER (*Zeitsch. physiol. Chem.*, 1909, 63, 413—431).—An increase in the concentration of hæmoglobin in the blood was not observed with certainty at an elevation of 3000 to 4560 metres. In severe muscular work, a noteworthy dilution of the blood occurs. Profuse sweating leads to a decrease of chlorides in the body, which on the days following it, is succeeded by retention of chlorides.

The loss of chlorides may lead to a cessation of hydrochloric acid secretion in the stomach. W. D. H.

Neutrality Equilibrium in Blood and Protoplasm. Lawrence J. Henderson (*J. Biol. Chem.*, 1909, **7**, 29—36).—The power of proteins to preserve neutrality in solution, which is regarded as of great importance by Brailsford Robertson, is great, but under conditions obtaining in the organism, is not comparable with that of the inorganic constituents of blood and protoplasm. There is no proof that more than a small portion of the carbon dioxide liberated from the blood in the lungs comes from sodium hydrogen carbonate which has given up its sodium to proteins, according to a simple reaction which is reversed in the tissues. It is improbable that this is the chief reaction involved unless indirectly through the heterogeneous equilibrium between red corpuscles and plasma, including the movement of chlorine, ionised or otherwise, across the red corpuscle wall and the consequent liberation and fixation of carbon dioxide in the plasma. W. D. H.

Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids. Giuseppe Buglia and L. Karczag (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 474—481).—Investigation of the influences exerted by the various tartaric acids on the coagulation by heat of dialysed blood-serum (compare this vol., ii, 52) shows that the action of these acids is due mainly to the hydrogen ions when the acids are present in very small concentrations; when, however, the concentrations are relatively high, the actions are determined principally by the stereochemical configurations. So that, only when the concentrations are high, are differences observable between the actions of the different acids. The actions of the various tartaric acids on muscular proteins (gastrocnemius muscle of the frog) are, in general, analogous to those exerted on the neutral protein of dialysed blood-serum. Both in accelerating the coagulation of the blood-serum and rendering it non-coagulable, and also in determining the velocity of coagulation (contraction) of muscle by heat, the *l*-acid is more effective than the *d*-acid. T. H. P.

Reversed Activity of Tissue Extract made at High Temperatures. Bertram J. Collingwood (*Proc. physiol. Soc.*, 1909, xiv—xv; *J. Physiol.*, **39**).—At 115° a tissue extract loses its power to accelerate blood-coagulation. If the undissolved residue is extracted at this temperature, an anti-coagulant is formed. W. D. H.

Glycolysis. I. The Susceptibility to Alkali of Dextrose. Leonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1910, **23**, 364—369).—The difficulties of measuring glycolysis in the blood are mainly two; one, the difficulty of estimating sugar in a protein-rich fluid can be overcome by the authors' method; the other is the supposed loss of sugar due merely to the action on it of the alkali of the blood and tissues. It has been known for a long time that sodium hydroxide and sodium hydrogen carbonate cause dextrose to disap-

pear from solution; this is confirmed—the optical activity gets less and less, it being largely due to conversion into lævulose or mannose. But the alkalinity of blood is not that which can be estimated by titration, but depends on the concentration of hydroxyl ions, and can be imitated by mixtures of primary and secondary sodium or potassium phosphates; such solutions cause no change in the optical activity or concentration of sugar in solution; the disappearance of sugar due to mere alkalinity of the blood is therefore a negligible factor.

W. D. H.

Physico-chemical Behaviour of Uric Acid and its Salts in the Blood. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, **63**, 455—477).—Uric acid can only exist in the blood as monosodium urate. In pure water this salt exists in two isomeric forms; the first (α-salt) is more soluble, but more unstable, than the other form (b-salt); the same is true for artificial and probably also for natural serum. Under certain conditions, for instance, in gout, the blood can be oversaturated with the urate, and this may lead to its deposition in the tissues, but no specific affinity between cartilage and uric acid exists. W. D. H.

The Behaviour of the Anti-Substances of the Blood-Serum Towards Solvents and Other Reagents. K. KAWASHIMA (*Biochem. Zeitsch.*, 1909, **23**, 186—192).—The anti-trypsin and anti-rennet action of the blood-serum was investigated. The serum was dried in a vacuum to a powder. The anti-properties were not appreciably altered by extraction with ether or ethyl alcohol. The anti-rennet action was, however, appreciably diminished by treatment with methyl alcohol, the anti-tryptic action being diminished by the same treatment only to a slight extent. The anti-rennet cannot be detected in the methyl alcohol. A small amount of the anti-trypsin dissolves in a mixture of equal parts of methyl alcohol and water. Acetone appears to render the anti-substances insoluble in water. Hydrogen peroxide and salicylaldehyde injure both anti-substances. Treatment with acids, alkalis, and ferments appears to exert no action on them. S. B. S.

The Proportionality of Proteolytic and Rennetic Action of the Gastric Juice of Man and Dog in Normal and Pathological Cases. TH. J. MIGAY and W. W. SAWITSCH (*Zeitsch. physiol. Chem.*, 1909, **63**, 405—412).—The experiments recorded show that the two properties of gastric juice referred to vary directly the one to the other both in normal and pathological conditions, and therefore support Pawloff's view that both are due to one and the same enzyme.

W. D. H.

Partial Transformation of Alimentary Fatty Matter into Mannitols by Peptic and Pancreatic Digestion in vitro. ÉMILE GAUTRELET (*Compt. rend.*, 1909, **149**, 1150—1151).—The author cites the results of experiments, from which he draws the conclusion that the artificial acid-peptic digestion of fatty materials, such as olive oil, butter, or tallow, converts these into *l*-mannitol,

whilst, when the digestion is pancreatic, in an alkaline medium the mannitol produced is dextrorotatory. The amount of mannitol produced depends largely on the state of division of the fat, and in the case of peptic digestion on the acidity of the solution.

W. O. W.

Action of Heat on Dry Pancreatic Extract. EUGÈNE CHOAY (*J. Pharm. Chim.*, 1910, [vii], 1, 10—16).—Various observers have recorded that the proteolytic activity of dry pancreatic extract is but little affected by exposure to a temperature of 100°. The author finds that exposure to a temperature of 80° or 100° during one or two hours scarcely affects the activity of the amylase, lipase, or trypsin present in pancreatic ferment, but that at 120° the activities of all three enzymes are rapidly paralysed. Of the three, the amylase seems to be affected least by heat. In solution, on the contrary, all three enzymes are rapidly affected by heat, thus mere desiccation of pancreatic ferment at 40° to 50° reduces the activity of the amylase by three-quarters and that of the lipase by one-half.

T. A. H.

Fat Cleavage by Pancreatic Juice. I. ÉMILE F. TERROINE (*Biochem. Zeitsch.*, 1910, **23**, 404—427. Compare Abstr., 1909, ii, 497).—Addition of mono- or di-glycerides does not influence the cleavage of triglycerides by pancreatic lipase. The addition of oleic acid to an emulsion of olive oil hinders the process of saponification, but the addition of glycerol increases the rate of cleavage. This is specially the case for emulsions and solid fats; the action of glycerol is slight or absent in the case of fats soluble in water (mono-butyrin, triacetin). Any viscous substance (gum, egg-albumin) has a similar favourable action. The optimum temperature for pancreatic lipase is 40°, but cleavage occurs even at 0°. Warming the lipase to 45° lessens its power, and to 65° destroys it. In presence of bile salts, it is more easily affected by rise of temperature. The enzyme acts in a neutral, but better in a faintly alkaline, medium (optimum *N*/150); it is lessened in acid or strongly alkaline media.

W. D. H.

Concentration of Anti-substances in the Body-fluids of Normal and Immune Animals. J. R. GREER and F. C. BECHT (*Amer. J. Physiol.*, 1910, **25**, 292—309).—A research on similar lines to that carried out by Hughes and Carlson (Abstr., 1908, ii, 304), determining the amount of hæmolysins, agglutinins, precipitins, etc., in the various fluids of the body.

W. D. H.

The Purine Bases of the Bone-marrow. H. THAR (*Biochem. Zeitsch.*, 1909, **23**, 43—44).—The following yields of purine bases were obtained from 1000 grams of bone-marrow: guanine 0·3125, adenine 0·1710, hypoxanthine 0·0724, xanthine 0·02875 gram.

S. B. S.

The Sugar Destructions in Animal Organisms which are Measurable by the Polarimeter. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1909, **23**, 324—328. Compare Abstr., 1908, ii, 714).—Extracts of liver and pancreas do not cause changes in the

rotation of lactose solution, such as the author has already shown occurs when this sugar is kept with milk. He has also followed the changes in the rotation of solutions of other sugar solutions when kept with animal fluids or extracts of organs. Dextrose solutions were not changed by extracts of organs. Urine caused a slight diminution of the rotation of lactose solution, and also of dextrose solution. The reducing powers in these cases were only slightly, if at all, altered.

S. B. S.

Lactic Acid in the Autolysed Dog's Liver. TADASU SAIKI (*J. Biol. Chem.*, 1909, **7**, 17—20).—The lactic acid in autolysed dog's liver is largely sarco-lactic [*d*-lactic] acid, as in other organs. A small amount of fermentation-lactic acid is also observed even in the sterile condition.

W. D. H.

The Action of Mercury Salts on Autolysis. MARCO TRUFFI (*Biochem. Zeitsch.*, 1909, **23**, 270—274).—It has been shown that mercury salts promote the autolytic process, and the author has determined the optimal quantities for various salts.

S. B. S.

Cholesterol Esters in the Human Epidermis and their Reactions. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1910, **23**, 361—363).—The cholesterol ester of palmitic acid was separated from human epidermis, which was identified by its melting point, colour reactions, and elementary composition.

W. D. H.

The So-called Fat of Tissues and Organs. HUGH MACLEAN and OWEN T. WILLIAMS (*Bio-Chem. J.*, 1909, **4**, 455—461).—The presence of "masked fat" in cell protoplasm is now recognised as a fact of physiological and pathological importance. The yield of "fat" differs with the extracting agent employed, according to its disintegrating action on protoplasm or the fat-products. The main material in the so-called fat is phosphatide, which may be free or combined. The organ chiefly investigated in the present research was the liver, but some details are also given of other tissues. The methods of extraction are also described.

W. D. H.

The Importance of Phosphatides for the Living Cell. II. WALDEMAR KOCH (*Zeitsch. physiol. Chem.*, 1909, **63**, 432—442. Compare Abstr., 1903, i, 301).—In colloidal solutions of phosphatides, reactions are observed similar to those which occur in physiological material. Carbon dioxide and ammonia in small concentration affect lecithin emulsions, leading to alteration in its hydrogen-ion and hydroxyl-ion concentration. Phosphatides play their part in the morphological and chemical differentiation of cells, especially in regard to the formation of membranes

W. D. H.

The Relationship of Diastatic Efficiency to Average Glycogen Content in Tissues and Organs. HUGH MACLEAN (*Bio-Chem. J.*, 1909, **4**, 467—479).—Great variations occur in animals, even of the same species, in the diastatic efficiency of their tissues. Very often an

organ containing mere traces of glycogen (for instance, the lung) has a higher amylolytic power than the liver. Wohlgemuth has recently published similar results. There is, in fact, no definite correlation between glycogen content and diastatic efficiency in the case of adult tissues. W. D. H.

Chemico-physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÉ SCALINCI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 423—430. Compare this vol., ii, 56).—The authors have examined the influence exerted by sodium chloride on the imbibition of the crystalline lens of the dog in solutions of acids and of sodium hydroxide (compare Abstr., 1909, ii, 502). The imbibition in 0·2*N*-sodium chloride solution is increased slightly by acids and very considerably by sodium hydroxide. In the latter case, the velocity and magnitude of the imbibition are proportional to the concentration of hydroxyl-ions, whilst with acids the amount of imbibition is directly proportional to the concentration of hydrogen-ions, hydrochloric and acetic acids favouring imbibition rather more than sulphuric acid of the same concentration.

From these and previous results, it is evident that alkalis are the most potent agents influencing the imbibition of the tissues, and that the extent of the physiological imbibition of every living cell and fibre corresponds with a certain relation between the concentration of the neutral salts and that of the salts which in aqueous solutions have alkaline reactions owing to hydrolytic dissociation. For a given concentration oi hydroxyl-ions, the imbibition of the crystalline lens or of the tissues is greatest in absence of neutral salts. The absorption of the lens, muscles, etc., should be less in a solution of barium or calcium hydroxide than in one of sodium or potassium hydroxide of the same concentration. T. H. P.

The Iodine Complex in Sponges. HENRY L. WHEELER and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1909, 7, 1—10).—Drechsel's iodo-gorgonic acid from Gorgonian corals was shown to be 3 : 5-di-iodotyrosine by Wheeler and Jamieson (Abstr., 1905, i, 350). In sponges, also, it is now shown that the iodine is present in the same form. The common bath sponge served as the source of the material. The ease with which iodine enters into combination with the aromatic group suggests certain considerations respecting the function of iodine in proteins, some of which are commented on.

3 : 5-Di-iodotyrosine and the similar compound with bromine are precipitated by phosphotungstic acid, whilst tyrosine itself is not. It does not give the tyrosine reaction with Millon's reagent until after reduction. W. D. H.

The Theory of Urea Formation. ALBERT A. EPSTEIN (*Biochem. Zeitsch.*, 1909, 23, 250—261).—According to Schmiedeberg's theory, urea is formed in the organism from ammonium carbonate; according to the theories of Salkowski and Hoppe-Seyler, urea is formed by the addition of ammonia to a substance in which a nitrogen atom is already bound to a carbon atom (for example, cyanates). If the

Schmiedeberg conception is correct, then there is no limit (except the toxicity) to the amount of ammonia which can be converted in the organism into urea. If the other theories are correct, then there is a limit, as the amount of cyanate or other groups available for synthesis depends on the protein degradation. In the latter case, if the amount of nitrogen in the ammonium salt ingested exceeds that derived from protein, the excess of ammonia should be excreted in this form and not as urea. Experiments carried out on rabbits by the author, in which the nitrogen of the ammonium salt (lactate) administered exceeded that of the normal nitrogen output on a fixed diet, lead to the conclusion that there is no limit to the amount of ammonium salt which can be converted into urea. The results, therefore, support Schmiedeberg's theory. S. B. S.

The Origin of Lactose. CH. PORCHER (*Biochem. Zeitsch.*, 1910, **23**, 370—401).—If the mammary glands are removed in cows and goats immediately after parturition, glycosuria of variable intensity sets in rapidly, and lasts about twenty-four hours. A similar result follows amputation of the breasts in lactating animals. This is associated with hyperglycæmia; lactose is not present. Phloridzin injection in suckling animals produces glycosuria as well as in lactating and male animals. In the operation cases just referred to, the sugar is dextrose, which, in the absence of the mammary glands, is not converted into lactose. W. D. H.

Influence of Lactic Acid Ferments on Intestinal Putrefaction in a Healthy Individual. HELEN BALDWIN (*J. Biol. Chem.*, 1909, **7**, 37—48).—A full account of a prolonged series of observations on a man which showed that sour milk exerted no specially favourable influence on the subject's condition. The excretion of ethereal sulphates and phenol in the urine, and of indole and scatole in the fæces, was usually increased when the fermented milk was taken. W. D. H.

Experimental Glycosuria. V. The Distribution of Glycogenolytic Ferment in the Animal Body, especially of the Dog. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1910, **25**, 255—291. Compare Abstr., 1909, ii, 168).—Prolonged perfusion of the liver with isotonic salt solution does not lessen the power of the extracts of the organ to destroy glycogen; this is against the view that the action is due to lymph. The full amount of glycogenolysis is not obtained until the tissue cells are crushed in Buchner's press; the ferment responsible is therefore an endo-enzyme. This is termed glycogenase; it is most abundant in the pancreas, the liver and blood-serum (or plasma) come next, and then the kidneys, intestines, and muscles. The nutritive condition of the dogs used is not a factor in the activity, and the blood-serum from the pancreatic vein does not contain more of the enzyme than that from the carotid artery. The organs of pig, rabbit, and especially the lamb, are less active than those of the dog. W. D. H.

The Urorosein Reaction. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, **7**, 57—58).—Herter has shown that indoleacetic acid is the chromogen of urorosein, and that the reaction is obtained when nitrites are also present in the urine. Ciusa and Terni (Abstr., 1908, i, 763) state that one of the derivatives of cinnamylideneacetophenone, the α-oxime, when given to animals causes the appearance of the urorosein reaction in their urine. This was repeated in the present experiments with negative results. It is suggested that the previous animals had a trace of indoleacetic acid in their urine, and that the administration of the oxime was followed by the occurrence of nitrites, for it is known that hydroxylamine is converted into nitrous acid in the organism. W. D. H.

The Action of Saline Purgatives. ARTHUR F. HERTZ, F. COOK, and E. G. SCHLESINGER (*Guy's Hospital Reports*, 1909, **63**, 297—307). —Two views are held in regard to the action of saline purgatives; one, the more prevalent supposes that the salt attracts water into the intestine and so produces fluid stools; the other supposes that the salt is absorbed and the effect is due to a specific irritation by the absorbed salt of the intestinal neuro-muscular and secretory mechanism, leading to increased peristalsis and increased secretion. The present paper is an argument in favour of the latter theory. It is pointed out that the purgation often occurs within half an hour, and that Röntgen-ray pictures of the intestine show that what is taken by the mouth does not reach the cæcum until four hours later. This time is only very slightly shortened after a saline purge. Further, the watery contents which are increased consist of succus entericus, not simply of water; of the sulphate administered, the fæces show little, if any, increase, whilst into the urine the excess of sulphate passes very rapidly, showing that it has been absorbed. W. D. H.

The Estimation of Ferments in the Fæces. HANS URY (*Biochem. Zeitsch.*, 1909, **23**, 153—178).—The following data were determined: amount of fæces, total solids, weight of solids in aqueous extract, and the nitrogen in the total and the extract. The following ferments were quantitatively estimated in the aqueous extract: pepsin (by Volhardt's method), amylolytic ferment (by Wohlgemuth's method), the pancreatic ferment (by Volhardt's method), the lipase, the nuclease (by determination of the adenine yielded by thymus nucleoprotein), the maltase, and the invertin (by the usual polarimetric methods). The results were calculated in terms of 1 gram of dry substance or of 1 gram of nitrogen, except in the case of the pancreatic enzyme, which was calculated in terms of 0·01 gram of nitrogen. Pepsin was found to be always absent from fæces, and also lipase. Nuclease and maltase were present in the fæces after administration both of senna and magnesium sulphate, but absent in the normal fæces. After administration of the former drug, the ferments normally present in fæces (amylase, pancreatic ferment, and invertin) were in considerably increased quantities; this was not the case after magnesium sulphate administration. The author gives full details of his experimental methods. S. B. S.

Chemistry of Cancer. II. Purine Bases, Creatine, and Creatinine. TADASU SAIKI (*J. Biol. Chem.*, 1909, 7, 23—26).—After removal of fat and lipoids from a number of cancerous tumours, the residue was hydrolysed with sulphuric acid, and purine bases determined by the Krüger-Schmid method. The following figures are given: uric acid, 0·024%; adenine as picrate, 0·032%; hypoxanthine as nitrate, 0·0034%; guanine and xanthine are only present in traces; this suggests the presence of guanase and oxydase, and the absence of adenase, as in other human tissues. Creatine and creatinine were determined by Folin's method; the creatinine present amounted to 0·016% of the fresh tissue; creatine was practically not present.

W. D. H.

The Influence of Certain Alcohols, Hydroxy- and Amino-acids of the Aliphatic Series on the Sugar and Nitrogen Excretion in Phloridzin Diabetes of the Dog. I. PAUL HÖCKENDORF (*Biochem. Zeitsch.*, 1909, 23, 281—303).—To starving dogs receiving phloridzin injections, various alcohols, amino-acids, and other substances were administered, and the alterations caused in the nitrogen and sugar excretions were noted. It was found that the administration of those alcohols which contain an uneven number of carbon atoms causes, almost always, an increased sugar excretion. In the case of propyl alcohol this increase is not regular. The alcohols with three and five carbon atoms caused a diminution of the nitrogen output. The alcohols with an even number of carbon atoms did not cause an increased sugar excretion; neither did *n*-valeric acid. In this case both the sugar and nitrogen excretion were somewhat diminished. Fermentation-lactic acid caused a slight increase of sugar excretion and diminution of nitrogen excretion; *d-l*-alanine caused a slight increase in the sugar, and also an increase in the nitrogen. Olive oil caused an increase in the nitrogen output.

S. B. S.

Phloridzin Diabetes. I. A. ERLANDSEN (*Biochem. Zeitsch.*, 1910, 23, 329—360).—Phloridzin glycosuria is not regarded as a primary hepatogenous or renal production of sugar, and so Minkowski's theory is held to be untenable. It originates owing to the passage of phloridzin through the kidney, calling forth there an abnormal elimination of sugar by that organ, which is probably a true secretion. The sugar in the blood is removed in this way, but as the amount of sugar in the carotid blood does not diminish, it is necessary to suppose that a secondary compensatory sugar production occurs in the liver, as Bang has proved to be the case. The maximal amount of sugar in the urine occurs simultaneously with the maximum of phloridzin excretion, and it ceases at the same time as, or shortly after, the excretion of phloridzin ceases.

W. D. H.

Gout. F. GUDZENT (*Biochem. Zeitsch.*, 1909, 23, 275—277).—Polemical. The author contends that the conclusions of Bechhold and Ziegler (Abstr., 1909, ii, 916) are unjustified, as it is theoretically impossible for uric acid to exist as such in serum. It

must exist in the form of a sodium salt which will form supersaturated solutions, the degree of supersaturation of which will depend on rate of formation and other circumstances. He holds, also, that the conclusions of these authors are unjustified, because the analyses are incomplete, no account having been taken of the carbon dioxide tension of the solutions, and that it is impossible to entirely free the deposits analysed from serum and other substances. The author also states that other physico-chemical laws have not been taken into account in the investigations criticised. S. B. S.

The Influence of Alcohol on the Quantity of Phosphatides in Animal Organs. NADINE SIEBER (*Biochem. Zeitsch.*, 1909, **23**, 304—323).—The phosphatides were estimated in the organs of animals which had received alcohol, and in those of control animals which had received no alcohol, and had been kept under otherwise similar conditions. The organs of the former showed a smaller lecithin content than those of the latter, the diminution varying from 0·57% in the stomach wall to 11% in the brain, these numbers being the mean of several experiments. S. B. S.

The Chemical Constitution and Physiological Action of Alcohols and Acids. II. JACQUES LOEB (*Biochem. Zeitsch.*, 1909, **23**, 93—96. Compare Abstr., 1909, ii, 168).—The minimum quantities of alcohols necessary to convert negatively heliotropic copepoda into positively heliotropic organisms were determined. The higher the atomic weight of the alcohol, the greater was the activity. The same result was also obtained with daphnia. The narcotic effect was similar to the heliotropic effect. The heliotropic action of the acids is much stronger than that of alcohols. Hydrochloric, nitric, and sulphuric acids have about the same action as formic acid. The increased action of the fatty acids with higher molecular weights is not so marked as in the case of the alcohols. S. B. S.

The Fate of Histidine in the Body of the Dog. KATHARINA KOWALEWSKY (*Biochem. Zeitsch.*, 1909, **23**, 1—4).—The ingestion of histidine hydrochloride caused an increase in the acidity in the urine (even when sodium carbonate was administered), and a large increase in the total nitrogen and ammonia output in the urine, the ratio of ammonia to total nitrogen being also increased. The results indicated degradation of the body proteins. Methyliminazole acted toxically when administered to a dog. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Action of Sodium Benzoate on the Multiplication and Production of Gas by Various Bacteria. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1909, 7, 59—67).—Food preparations containing 0·1% of sodium benzoate nearly always contain small numbers of bacteria,

chiefly of the spore-bearing kind. In dextrose bouillon, the same percentage only slightly inhibits *Bacillus coli* and other intestinal bacteria. Gas production may, however, be considerably hindered. When mixed fæcal bacteria are introduced into dextrose bouillon containing 0·1 to 0·2% of sodium benzoate, the bacteria are unequally inhibited. In general, the organisms of the *Bacillus coli* type are more inhibited than cocci. W. D. H.

Decomposition of Nitrates by Bacteria. S. A. SEWERIN (*Centr. Bakt. Par.*, 1909, ii, **25**, 479—492. Compare Abstr., 1909, ii, 479)—Denitrification experiments with *Bacillus pyocyaneus* and *Vibrio denitrificans* showed that both microbes can frequently utilise dung, straw, and urine as a means of increasing denitrification in a marl, whilst in a black soil these substances were not utilised, although the microbes grow readily in the soil without manure. In one experiment the addition of a very large amount of dung (8%) resulted in a reduction of the amount of nitrate by 17% when the soil was inoculated with *Bacillus pyocyaneus*, but no effect was produced with *Vibrio denitrificans.* N. H. J. M.

Alcoholic Fermentation in the Presence of Sulphurous Acid. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim. sucr. Dist.*, 1909, **27**, 561—562).—The author does not agree with the statement made by Martinand (Abstr., 1909, ii, 823) that yeasts do not ferment sugar solutions in the presence of sulphurous acid. Pure yeasts which the author employed in his experiments became acclimatised to the presence of this acid. It is also pointed out that the beer yeast used by Martinand does not under ordinary conditions readily ferment sucrose in acid solution. W. P. S.

The Influence of Fermented Sugar Solutions on the Respiration of Wheat Seedlings. S. KOSTYTSCHEFF (*Biochem. Zeitsch.*, 1909, **23**, 137—142).—Dextrose solutions were fermented by zymin until they no longer exerted a reducing action on Fehling's solution; the alcohol was then distilled off. Seedlings soaked in such solutions showed an increased output of carbon dioxide, equivalent to 142% in twelve hours, as compared with seedlings which had been soaked in water. No increased alcohol production could, however, be detected, and the author assumes that the action is due to increased normal respiration, and not to alcoholic fermentation; the amount of oxygen used up, furthermore, does not increase in the same ratio as the carbon dioxide production. S. B. S.

The Influence of Mineral Salts on the Respiration of Germinating Seeds. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1909, **23**, 193—214).—The authors give the results of some preliminary investigations of the action of various salts on the seeds of *Lupinus angustifolius*, *Zea mais*, and *Pisum sativum.* The solutions investigated include Knop's solution and magnesium sulphate, potassium dihydrogen phosphate, potassium nitrate, magnesium sulphate, and other salt solutions, and also of solutions containing mixtures of salts. In each case the

output of carbon dioxide was measured and compared with the output of the same seeds grown in pure water. The results are expressed as the number of mg. of carbon dioxide expired per hour by one hundred seeds. The action of the salts was not the same on all the varieties of seed tested, and depends, perhaps, on the mineral content of them. Attention is called to the possible antagonistic action of various ions, such as has already been observed in other biological processes.

S. B. S.

The Part Played by Oxygen in the Formation of Protein in Plants. W. ZALESKI (*Biochem. Zeitsch.*, 1909, 23, 150—152).—The author has already shown that there is a considerably greater formation of proteins in the bulbs of *Allium cepa* which have been punctured as compared with intact bulbs (Abstr., 1901, ii, 619; 1902, ii, 348). He now extends this observation to pea seeds. A control was dried at 60—70°, and two other similar portions were kept, one in dry air, and the other in a dry oxygen-free atmosphere. The two latter portions contained more protein than the former, the portion which was kept in presence of oxygen containing the largest quantity of the three. There was no change in the amount of total nitrogen. The analyses were carried out by Stutzer's method. The author attributes the increased protein formation in oxygen to the increased energy supply to the seeds, and he assumes, therefore, that the action is only indirect.

S. B. S.

Selective Absorption of Ions by Roots. ENRICO PANTANELLI and M. SELLA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 481—488).—By means of plantlets of dwarf *Cucurbita pepo*, the authors have investigated the selective action of the absorptive epithelium of the roots on the anions and cations of various salts. The results confirm the capacity of this membrane of functioning as a septum unequally permeable for different ions, the amounts of the latter absorbed for various salts being given, in mg.-ions, in the following table:

	KCl.	$CaCl_2$.	K_2SO_4.	$CaSO_4$.	KH_2PO_4.	$CaHPO_4$.
Cation	23·38	0	11·6	0	1·15	1·10
Anion	30·68	51·39	18·07	1·98	49·04	78·93

In the case of the four soluble salts, potassium chloride, calcium chloride, potassium sulphate, and potassium dihydrogen phosphate, the amounts of carbon dioxide emitted by the young roots were determined, but on comparing these amounts with those of the cations remaining in excess, no general rule is observable. With calcium sulphate and the phosphate $CaHPO_4$, however, it appears that, the more rapid the absorption of the anion compared with that of the cation, the more carbon dioxide is emitted by the roots. This phenomenon is based on, at least, the two following causes: (1) increase of the respiring surface and mass by the accelerated development of the roots produced by the alimentary and catalytic influences of the rapidly absorbed anions; (2) the direct influences of these anions on the respiratory activity.

T. H. P.

Nitrogenous and Mineral Composition of Ornamental Plants. ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. chim.*, 1910, [iv], 7, 31—37).—With a view to the preparation of appropriate compound and complete manures for garden plants, the authors have determined the amounts of nitrogen and mineral constituents present, per kilogram of fresh plant, in a large number of species grown for horticultural purposes. These are tabulated in the original. T. A. H.

Chlorophyll. VII. Comparative Investigation of the Chlorophyll of Different Plants. RICHARD WILLSTÄTTER, FERDINAND HOCHEDER, and ERNST HUG (*Annalen*, 1910, **371**, 1—32. Compare Willstätter and Benz, Abstr., 1908, i, 199).—The existence of two distinct chlorophylls has been definitely established by Willstätter and Benz (*loc. cit.*). Crystalline chlorophyll is now shown to contain two methoxyl groups, whilst amorphous chlorophyll, from determinations with phaeophytin, contains one phytol residue and one methoxyl group for each atom of magnesium; phaeophorbin, derived from crystalline chlorophyll, is likewise a dimethyl ester.

The primary object of this investigation was to ascertain the extent of the distribution of these chlorophylls in the vegetable world, the method employed being as follows: the chlorophyll is extracted from the dry material by means of alcohol, and converted as completely as possible by oxalic acid into the magnesium-free decomposition product; the latter is then hydrolysed quantitatively, the weight of phytol obtained being a measure of the phaeophytin and, consequently, of the amorphous chlorophyll present in the plant.

Determinations made with grass, plantain, and stinging nettle, collected from various localities and at different times of the year, indicate that the nature of the chlorophyll is not influenced by these factors, a result not in accord, apparently, with the conclusion drawn by Borodin from his investigations (*Bot. Zeit.*, 1882, **40**, 608).

The results of the analyses of the chlorophyll of seventy plants taken from thirty-six families are recorded. These show that phytol is distributed widely in nature; with the exception of one family (*Verbenacae*), of which only one variety was examined, representatives of all the families investigated have been obtained in which phytolester-chlorophyll preponderates. In six cases the proportion of phytol was small, namely, in *Stachys silvatica*, *Galeopsis versicolor*, *Galeopsis tetrahit*, *Datura stramonium*, *Verbena officinalis*, and *Scrophularia nodosa*; crystalline chlorophyll was isolated from the first four, also from *Lamium maculatum*, which with *Atropa belladonna* and *Salix* occupies an intermediate position. The distribution of crystalline chlorophyll indicated by these results does not appear to be as great as was deduced by Borodin (*loc. cit.*) and Monteverde (*Acta Horti Petropolitani*, 1893, **13**, 123).

The basic decomposition product obtained from the various preparations of phaeophytin from seventy plants is in the majority of cases principally a mixture of phytochlorin-*e* and phytorhodin-*g*; the latter compound is the principal decomposition product of phaeophytin from *Pinus silvestris* and *Betonica officinalis*, whilst it is not present in the

decomposition product of phaeophytin from *Urtica dioica* and *Salix*. Analyses of the basic compounds just mentioned point to a larger proportion of carbon to nitrogen than that represented by the formulæ given by Willstätter and Hocheder (Abstr., 1907, i, 780).

The proportion of chlorophyll in the leaves of various plants has been estimated colorimetrically by comparison of the alcoholic extract with a standard solution of crystalline chlorophyll; it is found to vary from 0·5% to slightly over 1% of the dry material, a value smaller than that given by Tschirch. W. H. G.

Adenium Hongkel, the Ordeal Poison of the French Soudan. EM. PERROT and M. LEPRINCE (*Compt. rend.*, 1909, **149**, 1393—1395).—An aqueous-alcoholic extract of the flowers of *Adenium Hongkel*, from Upper Senegal, showed intense toxic properties. By extraction with chloroform, a neutral, yellow, amorphous *substance* was obtained, agreeing approximately with the formula $C_{20}H_{31}O_8$. The substance has m. p. 84—85°, and is characterised by the reddish-violet coloration developed with sulphuric acid, and by its marked sternutative action. Physiological experiments suggest that it belongs to the group of cardiac poisons resembling stropanthine. W. O. W.

Presence of a Glucoside, which is Decomposed by Emulsin, in the Leaves and Twigs of Eremostachys laciniata. JOSEPH KHOURI (*J. Pharm. Chim.*, 1910, [vii], 1, 17—19).—The leaves and young shoots were extracted with alcohol, the solvent distilled off, and the residue dissolved in an aqueous solution of thymol. Of this solution, half was treated with invertase, when its optical rotation rose from −14′ to 36′. It was then boiled to destroy the invertase, and, on cooling, emulsin was added. Under the influence of this ferment, the rotation changed to +6′, indicating the presence of a glucoside. This deduction was confirmed by the similar action of emulsin on an aqueous solution of that portion of the alcoholic extract soluble in a mixture of alcohol and ethyl acetate. Determinations of the amount of reducing sugar formed indicated that the glucoside present has not been described previously. T. A. H.

A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and other Plants. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, [iv], **5**, 1096—1098).—See this vol., i, 91.

Oxidation Taking Place in Wines. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1910, **15**, 15—19).—In order to ascertain the action of various oxidising substances on wine, the author has made a number of experiments in which wine was treated with copper oxide, nitric acid, etc. Whilst simple æration for a period of five minutes was without effect on the different constituents of the wine employed in the experiments, the addition of 125 grams of cupric oxide to 1 litre of wine caused, after a lapse of five and a-half hours, a decrease in the quantity of non-volatile acids and of glycerol present, whilst the amount of volatile acids showed a slight increase. In the case of another wine, which was treated with 0·2% of 40% nitric acid, and the action allowed

to continue for four days, the quantity of esters originally present was trebled; the glycerol, however, was diminished to the extent of about 30%. This action of the nitric acid was still more marked after twelve days' contact. The author agrees with the opinion of other observers that the presence of small quantities of iron and manganese has an effect on the formation of aldehydes and esters; he is also of opinion that it is not necessary that these metals should be derived from the soil by the grapes and pass into the wine as organic salts. It is possible that accidental contact with a metal will result in sufficient of the latter being dissolved to play an important part in the oxidation processes taking place subsequently in the wine. As cupric salts have such strong oxidising properties, it is advisable not to use copper vessels for containing wine, as even traces of the metal when dissolved may lead to alterations in the character of the wine. W. P. S.

Disappearance of Sulphur Dioxide. HUBERT (*Ann. Chim. anal.*, 1909, 14, 453—454).—The author attributes the rapid disappearance of sulphur dioxide from wines, not to oxidation, but to the formation of a stable combination with substances of an aldehydic nature. This may be shown experimentally by adding to sulphited wines a little urotropine (hexamethylenetetramine); the amount of total sulphur dioxide is at once reduced. L. DE K.

Difference of Races and Individual Beets with Regard to their Composition. KARL ANDRLÍK, V. BARTOŠ, and J. URBAN (*Zeitsch. Zuckerind. Böhm.*, 1910, 34, 221—237).—Different races of sugar-beet, grown under the same conditions, show differences in composition, especially in the pure ash. The ash of roots with high percentage of sugar contains more calcium, magnesium, and phosphoric acid, and less sodium, than roots with low percentage of sugar; and they contain less alkalis to 100 parts of sugar.

Individual roots of different races, grown under the same conditions, may show essential variations in composition.

The amount of mineral constituents taken up per 100 parts of sugar varies both in individual roots of different races and of the same race. Roots with high percentages of sugar now take up less inorganic bases than was found to be the case by Walkhoff in 1874.

N. H. J. M.

Analytical Chemistry.

Manipulation of Small Precipitates. Qualitative and Quantitative Micro-chemical Analysis. FRIEDRICH EMICH and JULIUS DONAU (*Monatsh.*, 1909, 30, 745—757).—Micro-filters of paper are cut about 6—8 mm. in diameter, and placed on the thickened end of a capillary tube, which is cut square and polished. The tube acts as a funnel, and is placed in a suitable apparatus so that suction can be

applied. The application of a little vaselin to the rim of the filter, and its depression in the centre over the capillary by means of a glass rod, enables large drops to be filtered without danger of any loss owing to the liquid flowing off the paper. The precipitate is collected on the filter, washed, and placed in a sheet of platinum foil, which can be wrapped round it, and so prevent loss during drying, ignition, and weighing. A Nernst micro-balance was used for the weighings. A number of simple qualitative and quantitative estimations have been performed accurately and quickly in the manner described. E. F. A.

Apparatus for Filtering at a Constant Temperature. Alfred Eisenstein and Friedrich Ziffer (*Chem. Zeit.*, 1909, 33, 1330).—The apparatus consists essentially of a filtering tube surrounded by a constant-temperature jacket, the constant temperature being maintained either by a freezing mixture or by circulation of a liquid of known temperature. The filtering tube is made of three lengths of glass tubing of different widths, the two upper sections being contained in the constant-temperature jacket. A piece of platinum or copper wire gauze is placed at the lower joint, and on this can be placed the filter paper. The upper joint is ground to fit the elongation of the bulb of a thermometer, so that the top tube can be cut off from the middle one. If a substance is to be extracted at a constant temperature, it is placed in the middle section of the filtering tube, above the wire gauze; the upper joint it then closed by the thermometer, and the solvent poured into the top tube. When everything has attained a constant temperature, the thermometer is raised and the solvent allowed to percolate through the contents of the middle section.

The estimation of paraffin in paraffin shale, by Holde's method, is described to illustrate the working of the apparatus. T. S. P.

The Influence of Neutral Salts on Indicators. Leonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1909, 23, 61—67).—The influence of various neutral salts on the shade of the indicator colour was investigated, the hydrogen-ion concentrations being chosen for each particular indicator in which the latter is most sensitive, according to the determinations of Friedenthal. In some cases the addition of salt alters the nuance, so as to indicate increased acidity, in others, increased alkalinity. In the case of Congo-red, the authors think the change is due to the action of the salt in precipitating the dye; in other cases, they assume the change to be due to a different dissociation constant of the indicator in the new medium. The correction due to the presence of salts is negligible when the concentration reaches 1/8 normal (a concentration met with physiologically), except in the case of methyl-violet, Congo-red, and neutral-red. When necessary, a correction can be made in the Friedenthal method by adding salt to the control solution. The disturbing influence of proteins is much greater than that due to salts. S. B. S.

A New Sensitive Indicator. Dimethyl-Brown. M. Emmanuel Pozzi-Escot (*Bull. Assoc. Chim. Sucr. Dist.*, 1909, 27, 560—461).—The indicator is prepared by treating anthranilic acid in hydrochloric

acid solution with an excess of nitrous acid at the ordinary temperature; the diazo-substance obtained is combined with *p*-dimethylaniline, and the product is boiled with a large excess of hydrochloric acid and *p*-dimethylaniline hydrochloride. The solution is filtered while hot, and the filtrate is saturated with sodium chloride. The precipitate formed adheres to the sides of the vessel containing the mixture, and is washed rapidly with cold water. On dissolving the precipitate in alcohol, a solution is obtained which shows a brown coloration in neutral or acid aqueous solutions; alkalis change the colour to yellow.

W. P. S.

Systematic Detection of the More Important Acids. THADDEUS MILOBENDSKI (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1301—1306).—The method devised by Abegg and Herz (Abstr., 1900, ii, 436) for the separation and identification of acids, besides omitting several important radicles, possesses several disadvantages. Thus, the barium (group III) and calcium salts (group II) are very similar in their solubilities, and if excess of the reagent is used, the calcium precipitate always contains radicles belonging to group III; further, the detection of thiocyanates in the form $(FeCNS)_3$ masks the presence of iodides.

The author has modified the system so as to avoid these disadvantages. After giving a number of preliminary tests, he proceeds to the systematic scheme, the various groups being as follows:

(1) Strontium group, including phosphite, phosphate, arsenite, arsenate, sulphite, carbonate, tartrate, oxalate, fluoride, sulphate, and part of the borate. (2) Lead group, used if an iodide is present and containing iodide and sulphide; thiocyanate detected in the filtrate. (3) Zinc group, precipitated from the filtrate from group (1) and containing cyanide, ferro- and ferri-cyanide, and sulphide. (4) Silver group, comprising thiosulphate, iodide, bromide, chloride, and thiocyanate; chlorate and acetate detected in the filtrate. Details are given for the examination of the various group precipitates.

T. H. P.

The Detection of Hydrofluoric Acid in Presence of Fluorides. WALTER CRONHEIM (*Biochem. Zeitsch.*, 1909, **23**, 143—146).—As hydrofluoric acid is used as an antiseptic in foodstuffs, from which it is afterwards precipitated in the form of an insoluble salt, it is of importance to know whether traces of the acid remain in products which have been treated in this manner. As hydrofluoric acid is insoluble in alcohol and ether, whereas the salts are soluble, the two solvents are added to the sample under investigation. The fluorides are slowly precipitated from the supernatant liquid; the free acid remaining in solution is precipitated by calcium or barium hydroxide. In these two precipitates, fluorine can be detected by Hefelmann's (glass-etching) method, which can detect 1 part in 800,000.

S. B. S.

Action of Iodine on Sodium Dithionate or Trithionate in Solution. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1909, [iv], **5**, 1119—1121).—The object of this work was to ascertain whether

sodium thiosulphate could be estimated in presence of sodium dithionate or trithionate by titration with standard iodine solution. It was found that both the dithionate and the trithionate decolorise iodine solution when their solutions are warmed, but that in cold solutions, either neutral or acidified with acetic acid, the action is so slow that sodium thiosulphate can be safely titrated with iodine in their presence. T. A. H.

Volumetric Estimation of Selenious Acid in Alkaline Solution by Permanganate. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1909, **65**, 32—37).—None of the usual methods of titrating selenious acid are trustworthy under all conditions. Titration with permanganate in acid solution gives an uncertain end-point, but good results are obtained in alkaline solution according to the equation: $2KMnO_4 + 3SeO_2 = K_2O + 2MnO_2 + 3SeO_3$. The *N*/5-permanganate solution is prepared by dissolving 6 grams of potassium permanganate in 800 c.c. water, and adding 40 grams of potassium carbonate and 0·4 gram of potassium hydroxide; *N*/5-oxalic acid is used to standardise the solution. The selenious acid solution is made just alkaline with sodium hydroxide, titrated with permanganate, heating, and stirring well until the supernatant liquid is violet. It is then acidified with sulphuric acid and titrated with oxalic acid until all the manganese dioxide has dissolved. After cooling to 80—90°, the excess is titrated with permanganate.

Low results are obtained in the presence of chlorides, owing to the volatility of selenium chloride. Nitrates should be removed by evaporating with zinc sulphate and dilute sulphuric acid. The method is applicable to insoluble selenites. C. H. D.

Estimation of Total Nitrogen in Urine. HUGUET (*Ann. Chim. anal.*, 1909, **14**, 453).—Five c.c. of pure sulphuric acid are introduced into a 500 c.c. flask, which is then placed in an inclined position on a wire gauze and heated until sulphuric fumes appear. A mixture of 10 c.c. of urine and 25 c.c. of sodium persulphate solution (20 grams in 100 c.c.) is now added drop by drop, and the whole is then heated again until quite colourless. When cold, 10 c.c. of water and 2 drops of phenolphthalein are added, and the liquid is neutralised carefully with pure aqueous sodium hydroxide; D 1·26. After diluting to 100 c.c., an aliquot part is taken for the gasometric estimation of the nitrogen by the hypobromite method. L. DE K.

Source of Error in Estimating Ammonia. ÉTIENNE BARRAL (*Bull. Soc. chim.*, 1910, [iv], **7**, 8—9).—It was found that in using Schloesing's method for the estimation of nitrogen as ammonia, new block-tin worm condensers absorbed considerable quantities of ammonia, and accurate results were only obtained after the condensers had been used some time. Granulated tin absorbed only traces of ammonia, so that probably the loss was due to the presence of grease or tin oxides in the new condensers. T. A. H.

Estimation of Nitrogen in Nitrates by Reduction with the System Aluminium–Mercury. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1909, **149**, 1380—1381).—Not more than 0·5 gram of the

nitrate is treated in a Schloesing flask with 4 to 5 grams of aluminium turnings and a few drops of mercuric chloride solution; a little water is then added, and, after some minutes, when the action has ceased, a little alkali. After distilling off the ammonia, some sodium hypophosphite is added to decompose mercurammonium compounds.

The process has given excellent results with soils and manures.

W. O. W.

Detection of Arsenic Acid in Presence of Arsenious Acid by means of Magnesia Mixture. OSCAR LUTZ and R. SVINNE (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1488—1491).—Magnesia mixture being recommended by many authors as a means of detecting arsenic acid and its salts in presence of arsenious acid (only the ion of the arsenic acid being precipitated in the form of the salt,

$$MgNH_4AsO_4,6H_2O),$$

the authors have tested the reaction in presence of various proportions of ammonia and ammonium salts. The results show that, in presence of a sufficiently large amount of arsenious acid, the separation of arsenic acid by means of ordinary magnesia mixture is impossible. Further, aqueous or ammoniacal solutions of arsenious acid are less sensitive to the action of magnesia mixture than solutions of sodium and potassium arsenite. Qualitative separation may be attained under certain conditions of dilution, that is, for concentrations of the arsenious ion less than $M/200$ if ordinary magnesia mixture is employed, or less than $M/50$ if a large proportion of ammonium salts is present; but at such dilution, the lower limit of sensitiveness for arsenic acid may be passed. But, as the proportions of the two anions are usually unknown, and as the operation of dilution is too complicated for qualitative purposes, this method of separating the arsenic from the arsenious ion is not practicable. T. H. P.

Detection of Boric Acid in Butter and Milk. E. GAUVRY (*Ann. Chim. anal.*, 1910, **15**, 14—15).—A portion of the butter is melted with a small quantity of hot water, the aqueous layer is separated, filtered, and the filtrate is treated with a few drops of barium hydroxide solution. After the addition of a little alcohol, the mixture is subjected to centrifugal action, the clear solution is decanted, and the precipitate is treated with about 1 c.c. of hot concentrated oxalic acid solution. The barium oxalate, which dissolves in the excess of oxalic acid, is reprecipitated by the addition of alcohol and separated. The clear alcoholic solution is then evaporated after the addition of a few drops of an alcoholic solution of turmeric. As the evaporation proceeds, the edges of the liquid show a red coloration should boric acid be present, and eventually a red residue is obtained. The coloration is given by as little as 0·0001 gram of boric acid. In the case of milk, the test is applied to the ash.

W. P. S.

Ultimate Analysis of Coals Containing [Hydrated] Clays. A. LISSNER (*Chem. Zeit.*, 1910, **34**, 37—38).—If coals containing clay are submitted to the usual ultimate analysis, a large proportion of the

water collected is due to combined water contained in the clay, which a previous drying at 120° has failed to remove. The author, therefore, recommends the removal of the hydrated clay before proceeding to combustion.

The weighed portion of the sample is heated on the water-bath with a mixture of 2 vols. of fuming hydrofluoric acid and 1 vol. of hydrochloric acid; D 1·18. A twice or thrice repeated evaporation suffices to decompose the silicate. The residue is then treated with hot water, and collected on a dried and weighed filter. After drying at 100°, the filter and contents are submitted to the usual organic combustion. Allowance is made for the carbon and hydrogen yielded by the filter-paper, which may be taken as consisting of pure cellulose.

When dealing with samples chiefly consisting of clay, the process is as follows: The carbon is estimated in about 1 gram of the sample as usual. A similar quantity of the sample, which need not be weighed accurately, is then treated with acid as described, and collected on a filter. After drying for two hours at 100°, the carbonaceous matter is detached from the filter, and also submitted to analysis. In this way the proportion of hydrogen to the carbon is found, and the amount of carbon in the sample being accurately known, the hydrogen is found by a simple calculation. L. DE K.

Estimation of Carbon Monoxide in Air. E. GOUTAL (*Ann. Chim. anal.*, 1910, **15**, 1—7).—A portable apparatus is described for the estimation of carbon dioxide, the process employed depending on the oxidation of the monoxide to dioxide by means of iodic anhydride according to the equation: $5CO + I_2O_5 = I_2 + 5CO_2$. The iodic anhydride is contained in a tube, and is heated for some hours in a current of oxygen at a temperature of 200° before being used. During the estimation, the tube and its contents are heated to a temperature of 70° by means of a water-jacket, and the air under examination is drawn through the tube after having passed successively through wash-bottles containing acidified copper sulphate solution, potassium hydroxide solution, and concentrated sulphuric acid respectively. A filter, consisting of a tube filled with cotton-wool, may be placed before the wash-bottles. The volume of air drawn through the tube is ascertained by measuring the volume of water leaving the aspirator, and the rate of flow is regulated at about 1 litre per hour. The iodine liberated by the action of the carbon monoxide on the iodic anhydride is collected in a vessel containing either chloroform and water or potassium iodide solution; this vessel is placed between the exit end of the tube and the aspirator. The iodine collected is estimated by comparison with standard iodine solutions or by titration with standard thiosulphate solution. The process may also be employed for the estimation of the occluded carbon monoxide in steel; for this purpose, the steel is dissolved in potassium cupric chloride solution, and the gases evolved are passed, together with a current of pure air, through the tube containing the iodic anhydride.

W. P. S.

[Estimation of] Carbon Monoxide in Steels. E. GOUTAL (*Compt. rend.*, 1909, **149**, 1129—1131).—Compare this vol., ii, 129.

Titration by means of Borax in Presence of Glycerol. N. TANANAEFF and D. TSUKERMAN (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1469—1481).—Borax in presence of glycerol may be employed to titrate, not only pure alkali hydroxide, but also, on boiling, alkali hydroxide containing carbonate (compare Rupp, Abstr., 1907, ii, 194). The titration may be effected by adding alkali hydroxide to a solution containing borax and glycerol, and also by adding a solution of borax to one containing alkali hydroxide and glycerol. Titration with borax in presence of glycerol affords an excellent method of estimating alkali hydroxide in presence of carbonate. T. H. P.

Estimation of Zinc in the Presence of Iron. JAMES M. TAYLOR (*J. Soc. Chem. Ind.*, 1909, **28**, 1294—1295).—The process is based on the fact that a dilute neutral solution of zinc is precipitated by hydrogen sulphide with liberation of the acid, whilst ferrous salts are not affected.

Five to ten c.c. of the solution containing 0·1—0·3 gram of zinc are put into a flask, 20 c.c. of saturated solution of ammonium chloride are added, and any free acid is carefully neutralised with *N*/2-sodium hydrogen carbonate, with a drop of methyl-orange as indicator; 100 c.c. of saturated solution of hydrogen sulphide are now added, and the solution is titrated with *N*/2-sodium hydrogen carbonate, which should be added at first at the rate of 2 or 3 drops per second, and afterwards, when the precipitate turns greyish, more slowly. The end-point is reached when the colour changes to a decided chocolate (formation of iron sulphide). One c.c. of *N*/2-sodium hydrogen carbonate = 0·016 gram of zinc. In this process it is necessary that the iron should be in the ferrous state, and no other metals precipitable by hydrogen sulphide should be present. L. DE K.

New Volumetric Method for the Estimation of Copper. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1910, [iv], **7**, 9—17).—The process depends on the precipitation of the copper as cupric ferrocyanide, and the solution of this, in a solution of potassium cyanide, previously standardised against a copper solution of known strength. The change in colour from the reddish-brown of copper ferrocyanide to the faint greenish-yellow of potassium cuprocyanide is used as indicating the end-point.

The precautions to be observed are as follows: the solution titrated should contain the equivalent of not more than 0·1 gram of metallic copper, and must be exactly neutralised; it must be free from iron, lead, zinc, nickel, cobalt, or manganese, and should contain no ammonia or ammonium salts. The results are not influenced by the presence of tin, antimony, or arsenic, or by most organic acids, provided the latter are exactly neutralised. Exact details for using the method are given in the original, which also contains two tables of results obtained by its use. T. A. H.

Volumetric Estimation of Lead with Alkaline Permanganate. JULIUS F. SACHER (*Chem. Zeit.*, 1909, **33**, 1321—1322). —A criticism of Bollenbach's method (Abstr., 1908, ii, 68) for the

volumetric estimation of lead by means of alkaline permanganate. In Bollenbach's earlier experiments he found that one molecule of permanganate oxidised 3 atoms of lead, but later experiments (Abstr., 1909, ii, 1054) gave the number 3·34. The author shows that the latter figure is probably due to the sodium hydroxide used containing carbonate. He also finds that with increasing concentration of sodium hydroxide, the amount of lead nitrate necessary for the reduction of a given quantity of permanganate decreases, the temperature of experiment being 75—80°. Only when a series of estimations is carried out under exactly the same conditions do the results agree, and even then, the average error is 0·4% Pb, and is probably caused by varying temperature in different experiments; the lower the temperature the more lead nitrate is necessary for complete reduction of the permanganate. The action of varying concentrations of sodium hydroxide is probably due to its solvent effect on the lead sesquioxide, resulting in the re-formation of sodium plumbite. The method is quite untrustworthy for estimating the lead in materials containing lead sulphate. T. S. P.

Substitution of Bromine and of Iodine for Chlorine in the Separation of Cerium from the other Cerium Earths. PHILIP E. BROWNING and EDWIN J. ROBERTS (*Amer. J. Sci.*, 1910, [iv], **29**, 45—46).—The authors state that Mosander's process (passing chlorine through a solution of an alkali hydroxide containing in suspension the hydroxides of the cerium group) may be improved by substituting bromine for chlorine. At the first treatment some 50% of the admixed earths are removed, and, after two more treatments, a deposit of pure ceric hydroxide is obtained. It is important to remove the excess of bromine each time by heating on a water-bath.

Iodine also oxidises the cerium and causes the other earths to pass into solution, but the reaction is too incomplete to be of any analytical value. L. DE K.

Estimation of Chromium in Chrome Iron Ore. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1909, [iv], **5**, 1133—1136).—Three methods were investigated, using pure chromium sesquioxide as the analytical material.

In the first process, the oxide was fused with a mixture of sodium hydroxide and potassium nitrate, and the chromate formed, after cooling, was dissolved in water, the solution acidified with sulphuric acid, and boiled to decompose nitrites. It was then reduced by sodium sulphite, and the chromium precipitated with just sufficient ammonia. This precipitate was heated with sodium hydroxide and hydrogen peroxide solution, the excess of the latter being finally removed by prolonged boiling. The solution was then diluted to a known volume, and an aliquot portion titrated with potassium iodide and sodium thiosulphate (Abstr., 1909, ii, 96). This gave a result equivalent to 99·6% of the theoretical.

In the second process the sesquioxide was fused with a mixture of sodium peroxide and potassium hydroxide. The aqueous extract from this was filtered to remove a trace of silver derived from the crucible

used, boiled during forty minutes, diluted to a known volume, and the chromium in an aliquot portion determined as lead chromate, or by titration with sodium thiosulphate (*loc. cit.*). By this latter method, the process gave a result equal to 99·2% of the theoretical.

The Blodget-Britton process, depending on heating the sesquioxide with potassium chlorate and soda-lime, did not give good results owing to the difficulty of extracting all the chromate from the insoluble residue.

Chromite, even after grinding in a porphyry mortar, requires fusing four or five times in succession before it can be completely dissolved by either of the first two processes. For each part of the mineral, four of sodium hydroxide and eight of potassium nitrate, or five of sodium peroxide and eight of potassium hydroxide, are needed for each fusion. The aqueous extract of the fused product should be treated with a few drops of alcohol to remove any manganese present.

Both processes give equally good results with chromite, and the second is much more rapid, although it entails greater wear on the silver crucibles used. T. A. H.

Estimation of Tungsten in Tungsten-Steel. LUDWIG WOLTER (*Chem. Zeit.*, 1910, **34**, 2).—0·2—0·5 Gram of the sample, which need not be finely powdered, is fused in a covered platinum crucible with 0·5—1·5 grams of potassium pyrosulphate, and, when sulphuric fumes escape, the flame is removed for half a minute and another 4·5—13·5 grams of pyrosulphate are added in two portions. The mass is now heated gradually to redness and kept so for fifteen minutes. The lid is removed, and, when cold, the fusion is treated with 60—75 c.c. of water and boiled with 20 c.c. of hydrochloric acid. The tungstic acid is collected, washed with 10% ammonium nitrate solution, then dis solved in hot dilute ammonia, and evaporated in a weighed platinum crucible. On igniting the residue, pure tungstic acid is left.

Traces of tungstic acid retained in the acid liquid may be recovered by evaporating to dryness, heating the residue for one to two hours at 120—130°, and then boiling with dilute hydrochloric acid, which leaves the tungstic acid undissolved. If the presence of silica is suspected, this may be expelled by evaporating a few times with a few drops of hydrofluoric acid. L. DE K.

Separation of Vanadium, Molybdenum, Chromium, and Nickel in Special Steels. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1909, **149**, 1131—1132; *Ann. Chim. anal.*, 1910, **15**, 7—10).—The hydrochloric acid or nitric acid solution of the steel is heated to boiling and treated with a large excess of strongly alkaline sodium hypobromite. After boiling for some minutes, the insoluble iron and nickel hydroxides (also those of manganese and cobalt, if these metals are present) are filtered from the solution containing the chromate, molybdate, and vanadate of sodium. The precipitate is dissolved in dilute hydrochloric acid, and the solution again treated with alkaline hypobromite in order to get into solution all traces of chromium, molybdenum, and vanadium.

The iron and nickel are then readily separated, as also the chromium, molybdenum, and vanadium by the usual methods.

T. S. P.

Estimation of Antimony by Gutzeit's Method. CHARLES R. SANGER and EMIL RAYMOND RIEGEL (*Zeitsch. anorg. Chem.*, 1909, **65**, 16—24. Compare Sanger and Black, Abstr., 1908, ii, 64).—A special form of reduction apparatus is used, in which the gas evolved passes through a small chamber containing a disk of filter-paper saturated with lead acetate solution, which removes hydrogen sulphide and supplies the moisture required for the production of a regular antimony deposit. The mercuric chloride paper is cut into strips 6—7 cm. long and 4 mm. wide, and stored in the dark over calcium chloride. The reduction with zinc and hydrochloric acid is continued for thirty minutes, and the mercuric chloride paper, which is not coloured unless the antimony exceeds 0·07 mg., is developed by means of $N/1$ ammonia for five minutes. The length of the dark band thus produced is compared with a standard series of strips prepared with known quantities of antimony. Organic matter, except tartaric acid, must be absent, and the conditions of experiment must be exactly observed. The practical limit of sensitiveness of the method is about 0·001 mg. Sb_2O_3, which is a smaller quantity than can be recognised with certainty by Marsh's test.

C. H. D.

Analysis of Columbites and Tantalites. GABRIEL CHESNEAU (*Compt. rend.*, 1909, **149**, 1132—1135).—The mineral is dissolved by heating with a mixture of potassium hydrogen sulphate and sulphuric acid. The solid mass which is obtained on cooling is dissolved in water, the solution filtered, and the filtrate, after neutralisation with ammonium hydroxide, heated to boiling in order to precipitate the columbium and tantalum as pentoxides. The washed precipitate is digested for twenty-four hours with a tepid solution of ammonium sulphide, and then washed with cold 5% hydrochloric acid. While moist, it is treated with potassium fluoride and hydrogen fluoride in order to obtain the tantalofluoride and columboxyfluoride of potassium, which are then separated by the less solubility of the former in water.

The filtrates from the pentoxides of columbium and tantalum contain iron, manganese, etc., which are estimated in the ordinary way. The pentoxides also contain the silica and titanium dioxide present in the mineral; the silica is estimated by treatment of a known weight of the pentoxides with hydrofluoric acid.

The titanium is estimated colorimetrically by means of hydrogen peroxide, the colour not being affected by the presence of columbium and tantalum; the pentoxides containing the titanium dioxide are dissolved by treatment with a mixture of potassium hydrogen sulphate and sulphuric acid.

T. S. P.

Process for the Rapid Estimation of Alcohol. D. SIDERSKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1909, **27**, 562—563).—The method proposed depends on the complete miscibility of ether with concen-

trated alcohol. Twenty c.c. of the alcoholic liquid, wine for instance, under examination are placed in a stoppered tube, 10 c.c. of ether, D 0·724, are added, and 98% alcohol is run in from a burette in successive small quantities, the mixture being shaken after each addition. At first the ether separates out as a layer, but when sufficient alcohol has been added, the ether mixes completely with the alcoholic solution. The quantity of alcohol added is then noted, and is a measure of the amount of alcohol present originally in the sample. The burette employed is graduated so as to give directly the quantity of alcohol in the sample; it is a patented piece of apparatus, and it is quite possible that an ordinary burette graduated empirically may be used in its place. W. P. S.

New Method for Detecting Traces of Alcohols. E. DE STŒCKLIN (*Compt. rend.*, 1910, **150**, 43—45. Compare Abstr., 1910, i, 196, 198).—A description of a method for the detection of alcohols, based on their conversion into aldehydes by a peroxydase system. A few drops of the liquid to be examined are rendered very slightly acid with acetic acid. The mixture is then treated with two drops of a solution made by adding a ferric salt to a hot freshly prepared solution of quinhydrone and containing 0·1% of iron. A few drops of a 5% solution of hydrogen peroxide are added, and the mixture shaken. Schiff's reagent is employed to recognise the aldehydes formed; if present, ferric tannate is substituted for the iron-quinhydrone, and the operations repeated; under these conditions, glycerol gives no result. Deniges' reaction (Abstr., 1909, ii, 272—273) is recommended in conjunction with the foregoing as a sensitive test for glycerol. W. O. W.

Detection of Resorcinol by means of the Cyano-cupric Reaction. VOLCY-BOUCHER and J. GIRARD (*Ann. Chim. anal.*, 1910, **15**, 13—14).—When a neutral or slightly acid resorcinol solution is mixed successively with copper sulphate solution and a small excess of potassium cyanide solution, a bright green fluorescence is observed. The reaction takes place in the cold, and the reagents must be added in the order mentioned. The reaction is given by a solution containing as little as 0·1 gram of resorcinol per litre. W. P. S.

The Methods of Lecithin Estimation. JOSEPH NERKING (*Biochem. Zeitsch.*, 1909, **23**, 262—269).—Brain was submitted to fractional extraction with acetone, light petroleum, benzene, absolute alcohol, 85% alcohol, and ether, and the phosphorus determined in the extracts. These experiments led to no method for quantitatively separating the lecithin. Attempts were then made to quantitatively precipitate the lecithin from various solutions in organic solvents by means of pure acetone, and acetone to which various acids or salts had been added. It was found that egg-lecithin could be quantitatively precipitated from ethereal solution by acetone if, to the latter, a few drops of (cold) saturated alcoholic solution of magnesium chloride had been added. From other solvents and by the other methods tried (acetone solutions of tartaric acid, etc.), the precipitation was incomplete. S. B. S.

Volumetric Estimation of Sugars by K. Lehmann's Process. ERWIN RUPP and F. LEHMANN (*Arch. Pharm.*, 1909, **247**, 516—526).—Fehling's solution and a solution of the sugar are boiled for a suitable time, cooled, and poured into a mixture of potassium iodide, dilute sulphuric acid, and water, the liberated iodine being then titrated with $N/10$-sodium thiosulphate. Dextrose, lævulose, invert sugar, maltose, lactose, starch, dextrin, invert sugar in wine, maltose in beer, and lactose in milk have been estimated by this process or by slight modifications of it. C. S.

Separation of Sucrose and Lactose by the Bulgarian Ferment. L. MARGAILLAN (*Compt. rend.*, 1910, **150**, 45—47).—Bertrand has shown (Abstr., 1909, i, 623) that the lactic organism from curdled Bulgarian milk is capable of converting lactose almost quantitatively into lactic acid, but is without action on sucrose. It is possible, therefore, to estimate the latter in mixtures containing lactose or dextrose by treatment with the Bulgarian ferment, followed by inversion and determination of the reducing power. W. O. W.

The Method of Estimating Sugar in Urine. IVAR BANG and GÖSTA BOHMANNSSON (*Zeitsch. physiol. Chem.*, 1909, **63**, 443—454).—A defence of Bang's method (Abstr., 1907, ii, 136) against certain criticisms which have been made in reference to it. W. D. H.

Cammidge's Reaction. LÉON GRIMBERT and R. BERNIER (*J. Pharm. Chim.*, 1909, [vi], **30**, 529—536).—The authors state that Cammidge's reaction (*Lancet*, 1904) is obtained with all urines, and that the active principle formed by the hydrolysis with hydrochloric acid is glycuronic acid, which yields an osazone, m. p. 130—132°. L. DE K.

Detection of Reducing Substances in Urine. C. J. REICHARD (*Pharm. Zeit.*, 1909, **54**, 1007).—The author applies the gold-iodine reaction (Abstr., 1909, ii, 262) for the detection of reducing substances in urine, and also for their identification. The presence of reducing matters may be shown by placing in a test-tube 8 c.c. of water, 0·5 c.c. of neutral 1% sodium aurichloride solution, and 0·1 c.c. 1% potassium iodide solution, 1 c.c. of normal urine is next added, and the whole left for twelve to fifteen hours. The mixture first turns violet, and then gradually deposits a blue precipitate, which is examined microscopically. The precipitate may be purified by shaking the liquid, first with ether, and then, after evaporation of the ether, with chloroform. If sodium thiosulphate is cautiously added, the chloroform turns a violet-blue.

For the identification of urine, one drop of the gold solution, one drop of the potassium iodide solution, and two drops of the supposed urine are placed on an object glass and dried for twelve hours over sulphuric acid. The slide is then examined microscopically, and will

show the characteristic crystalline, blue iodine compounds of urea, uric acid, and creatinine. L. DE K.

The Quantitative Estimation of Amino-acids in Urine by means of Formaldehyde Titration. WALTHER FREY and ALFRED GIGON (*Biochem. Zeitsch.*, 1909, **22**, 309—315).—The ammonia was first driven off from the urine, and estimated by Spiro's modification of the Folin method (by means of a current of air after addition of barium hydroxide solution and alcohol, the ammonia being received in standard acid). The residue was diluted to a definite volume, in an aliquot part of which the amount of acid necessary for neutralisation with *N*/5-hydrochloric acid, using rosolic acid as indicator, was determined. Another aliquot portion was then neutralised with the experimentally-determined necessary amount of acid, and in this solution the amino-acids were estimated by titration with alkali after addition by neutral formaldehyde in the usual manner, phenolphthalein being employed as indicator. S. B. S.

The Quantitative Estimation of Amino-acids, Polypeptides, and Hippuric Acid in Urine by means of Formaldehyde Titration. VALDEMAR HENRIQUES and SOREN P. L. SÖRENSEN (*Zeitsch. physiol. Chem.*, 1909, **63**, 27—40).—The hippuric acid can be estimated by extracting the urine with ethyl acetate, hydrolysing the residue after evaporation of the solvent with hydrochloric acid, and then, after driving off the excess of mineral acid, estimating the glycine formed during the hydrolysis by the usual formaldehyde titration method. The polypeptides can be estimated by hydrolysing the urine, after separation of the hippuric acid, by hydrochloric acid, and then, after getting rid of excess of the mineral acid, estimating the amino-acids in the usual way. The difference between the number thus obtained and the amino-acid number obtained before hydrolysis gives a measure of the quantity of polypeptides present in the urine. The authors also give details as to the use of indicators in the ordinary formaldehyde titration method. S. B. S.

The Formaldehyde Titration of Amino-acids in Urine. TANZO YOSHIDA (*Biochem. Zeitsch.*, 1909, **23**, 239—244).—The author shows that the formaldehyde titration method of Sörensen and Henriques for estimating amino-acid nitrogen gives generally satisfactory results. Only in the presence of large quantities of ammonium salts are the numbers obtained appreciably too low. He gives the results of a number of analyses of both normal and pathological urines. S. B. S.

Detection of Biliary Acids, Lævulose, Glycuronic Acid, and Pentoses in Urine. ADOLF JOLLES (*Chem. Zeit.*, 1909, **33**, 1238—1239).—Polemical. A reply to the criticisms of Wittels and Welwart (Abstr., 1909, ii, 1057), in which the author recapitulates his methods and upholds their accuracy. L. DE K.

Detection of Biliary Acids [and Acetone]. RODOLFO FRITSCH (*Zeitsch. anal. Chem.*, 1910, **49**, 94—96).—Jolles's process, boiling with rhamnose and strong hydrochloric acid, is recommended instead of the Pettenkofer sugar-sulphuric acid test. The rose coloration, changing to a green fluorescence, is characteristic for biliary acids. These acids may be separated from amines by precipitating with a 3% solution of casein and sulphuric acid, and then extracting from the precipitate with absolute alcohol. If to dilute solutions of acetone are added a few drops of a 5% solution of rhamnose, and then an equal volume of strong hydrochloric acid, the liquid when heated turns a magenta colour, which is very permanent. 0·01 Gram of acetone in 1 c.c. of liquid may thus be detected. L. DE K.

Thiocyanates in Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1909, **33**, 1301).—The presence of thiocyanates in tobacco smoke may be proved by passing the fumes of a dozen cigars through two wash-bottles, each containing 100 c.c. of water, and adding to the mixed filtered liquids, copper sulphate and sulphurous acid. The precipitate is then collected and treated with aqueous sodium hydroxide; after acidifying with hydrochloric acid, the liquid will give the red colour with ferric chloride, disappearing on addition of mercuric chloride, or the aqueous solution may be mixed with zinc sulphate, which causes an abundant precipitate. The filtrate is then acidified with nitric acid, and, after adding copper sulphate solution, heated to 80°; the precipitate obtained is washed and treated with ferric chloride, when it will give a red coloration.

The amount of thiocyanate present may be estimated by passing the fumes of a dozen cigars through washbottles, each containing 100 c.c. of milk of lime. The united filtrates are evaporated and mixed with copper sulphate and excess of sulphurous acid. The copper thiocyanate is then converted by ignition into oxide and weighed as such, or Alt and Volhard's process—conversion of the thiocyanate into sulphate (*Zeitsch. anal. Chem.*, 1896, **35**, 315)—may be used. L. DE K.

New Test for Strychnine. PAUL MALAQUIN (*J. Pharm. Chim.*, 1909, [vi], **30**, 546—549).—One c.c. of a solution of a strychnine salt (about 1 : 1000) and 1 c.c. of pure hydrochloric acid are placed in a test-tube, and 1 gram of pure and clean zinc cuttings is added. After four minutes, the liquid is rapidly heated to boiling and then cooled. The solution is carefully poured down the sides of a test-tube containing 2 c.c. of pure sulphuric acid. Either at once or within a few minutes, a rose-coloured ring will be noticed; after a time the colour gradually spreads through the acid. The contents may also be shaken so as to accelerate the reaction. The colour is not altered on boiling, and in this way there is no danger of mistaking veratrine, which also turns red, for strychnine.

The colour is destroyed by potassium thiocyanate, but not by sulphur dioxide. Ammonia discharges the colour, but acids again restore it. None of the other alkaloids or glucosides (of which a list is given) show the reaction. Hydrogenation of strychnine may also

be effected in alkaline solution by means of sodium amalgam, but this operation is less convenient. Strychnine may be extracted by agitating its salts with ether in the presence of an alkali. The ether is then shaken with dilute hydrochloric acid, and, after warming to expel the ether, the liquid is treated with zinc as just directed. L. DE K.

Estimation of the Xanthine Bases in Cocoa and Chocolate. A. PROCHNOW (*Arch. Pharm.*, 1909, **247**, 698—711).—The author has tested the processes of Hilger and Eminger, of Dekker and Welmans, of Beckurts and Fromme, and Katz's modification of the last, for the estimation of theobromine and caffeine in cocoa and chocolate. Katz's process is the best, if carried out as follows: Six grams of powdered cocoa or 12 grams of powdered chocolate, 197 grams of water, and 3 grams of dilute sulphuric acid are boiled under a reflux condenser for thirty minutes in a tared litre flask. After the addition of 400 grams of water and 8 grams of magnesium oxide, the boiling is continued for one hour. Water, 30 to 50 grams, is added to compensate for that evaporated, the mixture is well shaken, and its weight, excluding that of the cocoa or chocolate, is determined. A portion of the liquid, five-sixths of the weight (corresponding with 5 grams of cocoa or 10 grams of chocolate), is filtered, and evaporated almost to dryness. The residue is dissolved in water, the solution is made up to about 25 c.c., treated with 25 drops of liquefied phenol, and extracted with chloroform in a Katz percolator for six hours. The chloroform in the extraction flask is evaporated, the phenol is carefully removed from the warm flask by the aid of the bellows, and the flask is dried until the weight is constant. C. S.

Estimation of Purine Nitrogen in Urine. STANLEY R. BENEDICT and TADASU SAIKI (*J. Biol. Chem.*, 1909, **7**, 27).—The Krüger-Schmid method of estimating purine nitrogen gives low and irregular results. Satisfactory results can, however, be obtained by first rendering the urine acid by adding 20 c.c. of glacial acetic acid to each 300 c.c. of urine. W. D. H.

New Reactions of Thiocarbamide. T. SATO (*Biochem. Zeitsch.*, 1909, **23**, 44—45).—The following reactions are described: coloration with acetic acid and potassium ferrocyanide (green changing to blue), with hydrochloric acid and potassium ferrocyanide, and with the ferrocyanide alone. The rate of development and disappearance of the colour varies in the three methods of carrying out the reaction. With sodium carbonate and ferrocyanide, a pink to violet colour gradually develops. This reaction is sensitive in dilutions of 1 in 10,000 to 1 in 20,000 of the urea derivative. S. B. S.

A New and Sensitive Reaction of Scatole. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1910, **23**, 402—403).—If 3 c.c. of scatole solution are mixed with 3 drops of methyl alcohol, and an equal volume of concentrated sulphuric acid added, a violet ring is formed at the place of contact; on shaking the fluids together, the whole mixture becomes violet-red. Dilutions up to one in five millions give the test. It is not given by tryptophan, indole, or by 2-methylindole. W. D. H.

Estimation of "Saccharin" [*o*-Benzoicsulphinide] in Various Foods. GUISEPPE TESTONI (*Zeitsch. Nahr. Genussm.*, 1909, **18**, 577—587).—The estimation of "saccharin" in foods and beverages is rendered somewhat complex by the presence of other substances which are extracted together with the "saccharin" by the usual solvents. The following methods of separating the "saccharin" from such substances are shown, from the results of actual experiments, to be trustworthy. Should the ether-extract contain benzoic acid in addition to the "saccharin," the extract may be heated at 110—115° until the whole of the benzoic acid has sublimed; the "saccharin" remains unchanged, and may then be weighed. The benzoic acid may also be removed by steam distillation. Another alternative is to precipitate the "saccharin" from an alcoholic solution of the ether-residue by means of silver nitrate; the silver compound formed has the formula $AgC_7H_4SO_3N$, and may be dried at 100° before weighing. In the case of wines, beer, aerated beverages, syrups, etc., the ether-extract will contain tartaric acid, citric acid, tannin, and other substances; these may be destroyed by oxidation with permanganate, and the "saccharin" then extracted from the evaporated solution. In the presence of salicylic acid, the ether residue may be weighed, and the salicylic acid then estimated in the usual way, the amount of "saccharin" present being found by difference, or the salicylic acid may be precipitated by means of bromine and the "saccharin" then extracted with ether, after removing the bromine compound by filtration. In cases where the ether-residue contains fatty substances, essential oils, etc., the oxidation process may be applied for the removal of any tartaric or citric acids present, and the sulphur then estimated in the purified residue of "saccharin"; or the "saccharin" may be hydrolysed by boiling with hydrochloric acid, and the ammonia formed then estimated. Pure "saccharin" yields 7·65% of ammonia.

The author finds that a mixture of equal parts of ether and light petroleum is the best solvent to use for the extraction of "saccharin" from its solution. W. P. S.

Estimation of Tannin [in Catechu]. G. C. A. VAN DORP and J. RODENBURG (*Chem. Weekblad,* 1909, **6**, 993—998).—The authors state that the only process which gives fairly satisfactory results in the assay of catechu is the process known as the Hunt-Loewenthal (titration with permanganate in presence of indigotinsulphonic acid before and after treatment with solution of gelatin).

The separation of non-tannin matters from tannins by means of hide powder, gives quite erroneous results. In one instance a sample of catechu gave 61·7% of tannin, but when another specimen of hide powder was used, only 34·3% was obtained. L. DE K.

The Detection of Blood-pigment by its Absorption of the Violet End of the Spectrum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1909, **63**, 478—483).—Details are given of the methods for studying the details of the absorption bands in the violet and ultraviolet region of the spectrum which hæmoglobin and its

derivatives exhibit, and which Gamgee, among others, called attention to. By suitable means an aqueous solution of blood examined in a thickness of 1 centimetre exhibits this absorption in dilutions of 1 in 4000 to 5000. W. D. H.

The Estimation of Pepsin by the Clarification of a Turbid Solution of Egg-white. S. HATA (*Biochem. Zeitsch.*, 1909, **23**, 179—185).—The egg-white solution is prepared by diluting egg-white in a mortar to five times the original bulk with water, filtering, heating at 60° for twenty minutes, and filtering again through muslin. A turbid solution is thereby obtained, which can be kept unchanged for several months. For the purposes of the test, this solution is again diluted with water to ten times its bulk. Into a series of test-tubes varying quantities of the pepsin-containing liquid are introduced, and diluted to 1 c.c. 0·5 c.c. of $N/10$-hydrochloric acid and 2 c.c. of the diluted suspension are then introduced, and the time of clarification is noted. The procedure is then similar to that employed in the ricin and edestin methods. The time of clarification is approximately inversely proportional to the dilution. S. B. S.

Employment of the Guaiacol Method for the Quantitative Estimation of Peroxydase. JULIUS BRUNN (*Ber. Deut. bot. Ges.*, 1909, **27**, 505—507).—In employing Ostwald's method (Abstr., 1907, ii, 976), quite fresh solutions of the resin must be used, as distinct amounts of peroxydase are formed in a few hours. A special defect is the use of drops of a strong resin solution instead of c.c. of a more dilute solution. The rate of the reaction should be determined, and not the final amount of colour.

The following method is recommended: A scale of colours of different intensity is prepared by diluting a blue water colour emulsion (Prussian blue with a little cadmium yellow and white). The back of the test-tube stand, which is placed in a window, is covered with tissue paper to avoid reflexions. The extracts in test-tubes are treated with hydrogen peroxide, and a little concentrated (golden-yellow) solution of guaiaconic acid (1 c.c. to 10—15 c.c. extract, to which 0·2 c.c. $H_2O_2/20$ had been added) poured on. The tubes to be compared are shaken simultaneously to mix the contents, and the increase in intensity of the colour observed at definite intervals and compared with the tube scale; the more rapid the coloration, the greater the amount of peroxydase (compare Euler and Bolin, Abstr., 1909, i, 863). N. H. J. M.

A Test for Mushrooms. M. LÖWY (*Chem. Zeit.*, 1909, **33**, 1251). —An aqueous infusion of *Agaricus campestris* gives with sulphuric acid, D 1·86, a deep violet coloration. The reaction is best carried out as a ring test. The colour disappears on warming. The author has not as yet succeeded in isolating the active principle. Infusions of other fungi do not give the reaction. L. DE K.

General and Physical Chemistry.

Pulfrich's Ratio between Volume Contraction and Refractive Power of Liquid Mixtures. EDMOND VAN AUBEL (*Compt. rend.*, 1910, **150**, 210—213).—Pulfrich has established the relationship: $(R - R_v)/R = q.(D - D_v)/D = qc$ for binary mixtures, where R denotes the refraction and D the density of the mixture, R_v and D_v the refraction and density respectively which the mixture would have shown had there been no volume change on mixing, whilst q is a positive constant. The author shows, by calculation from results obtained by Wintgen (*Thesis*, Bonn, 1908), that in the case of a mixture of aqueous solutions of tartaric acid and ammonium heptamolybdate, q is negative. W. O. W.

Molecular Refraction of Isomerisable Unsaturated Acids and their Salts. ARTHUR HANTZSCH and KURT MEISENBURG (*Ber.*, 1910, **43**, 95—105. Compare Brühl, Abstr., 1904, i, 969; 1905, i, 170).—The molecular refraction of nitroethane and nitropentane in ethyl alcohol and in potassium ethoxide solutions shows that the relationship between the two nitro-compounds in ethyl-alcoholic solution is perfectly normal. The difference is 13·83, and the value for $3CH_2$ is 13·80.

The results also show that the effect of the solvent on the refraction is not marked. Similarly, *p*-chloro- or *p*-bromo-phenol has practically the same molecular refraction in alcohol and in sodium ethoxide solutions.

A comparison of *p*-nitrophenol and *p*-nitroanisole proves that the phenol in *iso*butyl butyrate, acetone, and methyl-alcoholic solutions is a true phenol, the difference between the two compounds being practically the value due to CH_2. On the other hand, the *p*-nitrophenol in methyl alcohol and potassium methoxide solution shows a difference of 9·67 units; this undoubtedly indicates that the salts are derived from the *aci*-phenol. The following numbers give the increments in the mol. refractions of the three nitrophenols when transformed into their salts:

	p.	*o.*	*m.*
Mol. ref. D	9·68	4·26	1·80
Mol. ref. α	7·87	3·63	1·71

The molecular refraction and also the colour of solutions of *o*-nitrophenol indicate that it is partly converted into the *aci*-derivative.

With *o*- and *p*-benzaldehydes the following increments due to salt formation were obtained: ortho 3·20, para 4·88, results which point to the conclusion that the salts cannot be simple phenolic salts. It is pointed out that the relationships between colour and molecular refraction are not so simple as stated by Kauffmann (*Die Auxochrome*, p. 65).

The refraction of the azo-group, calculated from the value for azobenzene, is 13·95, whereas in ethyl diazoacetate it has the value 8·41. The values for *p*-hydroxyazobenzene, its ethyl ether, and its acetyl and propionyl derivatives agree with the normal hydroxylic structure for the free hydroxy-compound. The value for the hydroxy-compound is somewhat increased when ethyl alcohol is used as solvent, probably owing to the formation of an additive compound. The values for the salts show an increment of some 12 units. This is attributed not to structural molecular rearrangement, but as due to the play of subsidiary valencies, for example:

$$C_6H_4\begin{cases} N_2Ph \\ \\ OH \end{cases} \quad \text{and} \quad C_6H_4\begin{cases} -N_2Ph \\ \quad \vdots \\ OM \end{cases} \quad \text{or} \quad C_6H_4\begin{cases} N_2Ph \\ \quad \vdots \\ OM \end{cases} .$$

Similarly, the large increments noticed by Brühl in the salt formation of ethyl acetoacetate are not necessarily due to a structural alteration (enolisation), but may be due to the calling into play of subsidiary valencies.

It is pointed out that the molecular refraction of the salts is greater than that of the true enolic alkyl and acyl derivatives, and therefore this high exaltation can only be due to a further constitutive change due to subsidiary valencies:

$$\begin{array}{l} -C\cdot CO\cdot OEt \\ \;\| \quad \vdots \\ \;C\cdot OM \end{array} \quad \text{or possibly} \quad \begin{array}{l} \cdot C\cdot C(OM)\cdot OEt \\ \;\| \quad | \\ \cdot C\cdot O \end{array}$$

J. J. S.

Theory of Dispersion in Gaseous Substances. LADISLAS NATANSON (*Bull. Acad. Sci. Cracow*, 1909, 907—915).—Recent measurements of the dispersive power of nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulphide, sulphur dioxide, helium, and argon have been made use of to test a deduction made by the author from Lorentz's electronic theory of absorption. The calculations based on these data indicate with some degree of probability that the product $a.\Delta$, in which a is the number of dispersion electrons contained in a molecule of a gas, and Δ the constant in the equation: $(n^2+2)/(n^2-1)=\Delta(1/\lambda_0^2-1/\lambda^2)$, has the same value for all gases. The average value of $a.\Delta$ is $16{\cdot}3\times10^{-7}\text{cm.}^2$, and although in certain cases the experimental data of different observers differ widely, the author considers that sufficient evidence has been obtained to justify the conclusion that there is a close connexion between dispersion and valency. H. M. D.

The Long-waved Portion of the Spectrum of Titanium. PAUL FIEBIG (*Zeitsch. wiss. Photochem.*, 1910, 8, 73—101).—The author has made a detailed photographic investigation of the line and band spectra of titanium between λ 4200 and λ 7360. For the production of the spectrum, metallic titanium was introduced into a cavity made in the positive electrode of a carbon arc, and the requisite large dispersion was obtained by a Rowland grating having a radius of curvature of 6·6 metres and 20,000 lines to the inch. The measured wave-lengths together with the estimated intensities are

recorded in tabular form, and the results compared with those previously obtained by Thalén, Hasselberg, and Rowland.

H. M. D.

Investigation of the Sodium Spectra. HANS ZICKENDRAHT (*Ann. Physik*, 1910, [iv], **31**, 233—274).—The author has examined in detail the emission spectra obtained from the arc discharge between electrodes of different materials in an atmosphere of sodium vapour, and from the glow discharge under different conditions with and without an interposed spark gap. The consequent variations in the emission spectrum are described in detail.

In the second part of the paper, a summary is given of spectral observations relating to sodium, and these are discussed in reference to the author's measurements.

H. M. D.

Spectra of the Erbium Compounds and Stark's Valency Hypothesis. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Zeitsch. physikal. Chem.*, 1910, **71**, 312—324).—Stark (compare Abstr., 1908, ii, 574) has suggested a theory of valency based on the assumption that at the surface of a chemical atom there are positively charged spheres and minute negative electrons. When the atom enters into chemical combination, the lines of force from certain of the electrons become attached to the positive spheres on the other atom (saturated valency electrons); other electrons are not affected, their lines of force remaining attached to the positive spheres of their own atom (unsaturated valency electrons), while a third kind of electrons are affected in such a way that their lines of force are partly separated from the positive spheres of their own atoms (loosened electrons). According to Stark, the band spectra of the unsaturated valency electrons have their lower limit, at least in some cases, in the unattainable ultra-violet, $\lambda = 0{\cdot}06\mu$, the band spectra of the saturated valency electrons lie in the ultra-red above $\lambda = 0{\cdot}5\mu$. Hence in the visible region only the absorption due to the loosened valency electrons is of importance. The work of the authors on the spectra of erbium compounds supports Stark's theory.

The spectra of a number of solid anhydrous erbium salts were first measured at different temperatures by concentrating on them the light from the positive carbon of an arc lamp by means of a quartz lens, and examining the reflected light by means of a double prism instrument.

The spectra of erbium sulphide and chloride are very similar, and the change from chloride to oxide, and from oxide to sulphate, only brings about displacements of 1—3 λ in the absorption bands, so that the electrons concerned in the absorption are not the saturated ones effecting the combination between erbium and the other elements or groups. Similarly, the effect of temperature in displacing the absorption bands is very slight, whereas the chemical linkings produced by saturated electrons are very greatly affected by change of temperature. On the other hand, the addition of water to the salts produces a great alteration in the spectra, and it is suggested that this is due to hydrate formation with participation of the "loosened" electrons.

The saturated valencies may, therefore, correspond with Werner's "Hauptvalenzen" (principal valencies), the valencies due to the loosened electrons with Werner's "Nebenvalenzen" (subsidiary valencies).

From an examination of the groups of absorption bands of the binary anhydrous erbium compounds, the conclusion is drawn that the effects are produced by three "loosened" electrons, which, with the three "saturated" valencies, make a total of six, corresponding with Werner's co-ordination number. G. S.

Flame Spectrum of Iron at a High Temperature. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1910, **150**, 329—332. Compare Abstr., 1908, ii, 445, 547).—When sparks are passed through an oxygen-acetylene flame between iron electrodes, the spectrum shows fewer lines than the simple flame spectrum. The lines are more intense than those obtained with the oxy-hydrogen flame. Some of the lines are identical with those seen in the blue cone of the Bunsen burner. A comparison is made in tabular form showing the relative intensities of lines in the two flames. Lockyer's enhanced line, λ 3935·92, has been observed, but apart from this the lines are those characteristic of low temperatures, and are only visible in traces in the spectrum of the electric furnace. W. O. W.

Measurements in the Long-waved Spectrum. HEINRICH RUBENS and H. HOLLNAGEL (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 26—52).—The authors have examined the ultra-red rays of very great wave-length which are obtained as the result of selective reflexion at the surfaces of polished plates of crystals of sodium chloride, potassium chloride, bromide and iodide. The wave-length measurements were effected by means of a quartz interferometer, the ready absorbability of the long-wave rays necessitating, however, special arrangements in connexion with the details of the apparatus.

The residual rays, which were examined by a micro-radiometer after reflexion at four surfaces of the substance under investigation, form two bands of different intensity in the case of sodium chloride, potassium chloride, and potassium bromide. Although not definitely indicated by the data for potassium iodide, it seems probable that this grouping is also characteristic of potassium iodide. The mean wave-lengths of the bands are recorded for the first three salts, and it is found that these wave-lengths increase with the molecular weight of the salt.

As a result of the experiments with potassium bromide and iodide, the known spectrum has been extended by half an octave in the remote ultra-red region. The known part of the ultra-red region is thus approximately seven times as long as that of the visible spectrum. H. M. D.

Absorption Spectra of Various Salts in Solution and the Effect of Temperature on Such Spectra. HARRY C. JONES and W. W. STRONG (*Amer. Chem. J.*, 1910, **43**, 97—135).—A continuation of the work described previously (this vol., ii, 87). A review is given of recent spectroscopic investigations. Attempts have been made to obtain the Zeeman effect for the absorption bands of uranyl chloride

and neodymium salt solutions, but without success. It is hoped, however, that the Zeeman effect may be obtained with solutions of erbium salts.

In studying the effect of change of temperature on the absorption spectra of salts, spectrograms have been made of the spectra of aqueous solutions at various concentrations of cobalt chloride (alone and in presence of aluminium chloride and of calcium chloride), cobalt thiocyanate, nickel acetate and sulphate, copper bromide, copper chloride (alone and in presence of aluminium chloride and of calcium chloride), uranyl chloride, nitrate, acetate and sulphate, uranous chloride and sulphate, praseodymium chloride, neodymium nitrate and bromide, neodymium chloride (alone and in presence of calcium chloride), and erbium chloride.

The results are discussed in the light of the electron hypothesis.

It has been found that the effect of a rise of temperature of an aqueous salt solution is to increase the general absorption and also to broaden and intensify the bands, and that, as a rule, the increase of the general absorption is much greater in concentrated than in dilute solutions.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge as the temperature rises.

The uranyl chloride bands are shifted towards the red with rise of temperature. The uranyl acetate and sulphate bands are also slightly shifted, but those of the nitrate are not affected in this way.

In the case of the neodymium and erbium salts, the bands do not appear to be shifted as the temperature increases. In presence of calcium chloride, however, the neodymium chloride bands are shifted, and the bands become fainter with rise of temperature. E. G.

Restoration of Phosphorescence to Sulphides of the Alkaline Earths. DÉSIRÉ GERNEZ (*Compt. rend.*, 1910, **150**, 295—300).—Specimens of the phosphorescent sulphides of calcium, barium, and strontium were found to have lost their phosphorescence after an exposure of six years to moist air. This appeared to be due to oxidation to the sulphates, since the phosphorescence was restored by heating the substances in a current of hydrogen. The action of heat alone had very little effect on the phosphorescence.

W. O. W.

Photochemical Equilibria. III. Photochemical Equilibrium of Carbonyl Chloride. ALFRED COEHN and HANS BECKER (*Ber.*, 1910, **43**, 130—133. Compare Abstr., 1909, ii, 846).—Weigert (Abstr., 1907, ii, 835) has found that the dissociation equilibrium of carbonyl chloride at 500° is not affected by light; the action of the latter is simply to accelerate catalytically the attainment of equilibrium. His experiments are not conclusive, however, since glass vessels were used. The authors now find that when carbonyl chloride is passed through a quartz tube at the ordinary temperature, and at the same time submitted to the action of light from a mercury-quartz lamp, it is partly decomposed into carbon monoxide and chlorine. When 1 c.c. of carbonyl chloride passed through the quartz

tube (20 cm. long and 0·5 cm. in diameter) per minute, the amount of decomposition was 3·3—4%. The effect is chiefly due to the short ultra-violet rays, since when tubes of Uviol glass were used, which are only transparent to waves of greater wave-length than 265$\mu\mu$, the decomposition was only 0·46—0·5%. In ordinary glass tubes there was no decomposition.

In all the cases hitherto examined, namely, the photochemical equilibria of sulphur trioxide, hydrogen chloride, and carbonyl chloride, the actual equilibrium is affected only by ultra-violet rays. Rays of greater wave-length simply act catalytically on the attainment of equilibrium.

Experiments which are at present in progress show that water vapour is decomposed to a considerable extent by ultra-violet light.

T. S. P.

Chemical Action of Light. V. Photochemical Phenomena in Dye Solutions. FRITZ WEIGERT (*Ber.*, 1910, **43**, 164—172. Compare Abstr., 1908, ii, 5, 748, 914; 1909, i, 219, ii, 532).—In liquids exposed to the action of light, condensation nuclei are formed; these bring about local increases in concentration, and accelerate chemical reactions which do not take place in the dark. Proof of the formation of condensation nuclei is afforded by the fact that solutions of dyes exposed to light show an increased solvent action towards gases.

The dyes studied were uranin, erythrosin-G and -J, phloxin, methyl-violet, and malachite-green. These were enclosed in tubes with nitrogen, maintained at 15°, and exposed to the light from a mercury lamp. A manometer was arranged to indicate the gas pressure in the tubes, which were constantly shaken. The solubility of nitrogen in water is not affected by exposure to light. In the dye solutions a decrease in pressure took place, at first with constant velocity, but subsequently becoming slower. After keeping the tubes in the dark again, an increase in pressure was found, but the original value was never attained. A special differential-adsorptiometer was designed to remove the absorbed nitrogen by boiling the dye solution, but it was found only possible to recover a portion of the gas absorbed. The amount of dye present in solution is far too small to explain the increased solubility of the gas as due to the influence of the dye. Undoubtedly, condensation nuclei form, and the nitrogen condenses at their surface.

E. F. A.

Radioactivity of some Waste Springs in the Vosges. ANDRÉ BROCHET (*Compt. rend.*, 1910, **150**, 291—293).—Near the thermal springs of Plombières, Luxeuil, and Bains, there exist in the region of the Vosges some springs running to waste. The radioactivity, both of the gases and water, of these springs has been found to be high. Particulars are given of springs of the Chaudeau, Fontaines-Chaudes, and Chaudes-Fontaines or Reherrey.

F. S.

Radioactivity of Halogen and Oxyhalogen Compounds of Thorium. J. CHAUDIER and ÉDOUARD CHAUVENET (*Compt. rend.*, 1910, **150**, 219—221).—The radioactivity (α-radiation) of a number

of freshly prepared halogen and oxyhalogen compounds of thorium has been compared with that of thorium dioxide and thorium in a Curie electroscope. The powdered substances were sifted over plates 4 cm. in diameter, the weight of substance employed being varied up to 0·35 gram, for which the α-radiation is a maximum. In the latter case, the intensity of the radiation diminished as the atomic weight of the elements combined with the thorium increased. The substances arranged in descending order of activity were as follows: Th, ThO_2, $ThOF_2$, ThF_4, $ThOCl_2$, $ThCl_4$, $ThOI_2$, $ThBr_4$. As the weight of the substance employed is reduced, the differences in the relative activities of the compounds disappear. Below 0·01 gram all are of similar activity, indicating that the radioactivity is an atomic property of thorium. F. S.

The Action of the α-Rays on Glass. ERNEST RUTHERFORD (*Mem. Manchester Phil. Soc.*, 1909, **54**, v, 1).—Fine capillary tubes of soda-glass that had contained radium emanation show in transverse section a coloured region extending about 0·04 mm. from the inner wall of the capillary, corresponding with the range of the most penetrating α-rays of radium in glass. This confirms the correctness of Joly's explanation of pleochroic halos (*Phil. Mag.*, 1907, [vi], **13**, 381; 1910, **19**, 327). F. S.

The Absorption Law of β-Rays. W. WILSON (*Physikal. Zeitsch.*, 1910, **11**, 101. Compare *Proc. Roy. Soc.*, 1909, *A*, **82**, 612).—The former conclusion, that the exponential law of the absorption of β-rays is indicative of non-homogeneity of the rays which have a certain distribution of velocities, is reaffirmed and the criticisms of Hahn and Meitner (this vol., ii, 8) are replied to in detail. The conclusion is drawn that the β-rays suffer diminution of velocity in passage through matter. F. S.

Production of Helium by Radium. ERNEST RUTHERFORD and BERTRAM B. BOLTWOOD (*Mem. Manchester Phil. Soc.*, 1909, **54**, vi, 1—2).—The gases generated in eighty-three days from a solution of a barium-radium salt containing 0·2 gram of radium, which had been freed chemically from polonium and radium-*D*, were subjected to repeated absorptions with charcoal cooled in liquid air, and the unabsorbed part was found to consist of helium, essentially pure, in amount corresponding with a rate of production of 163 cu. mm. per gram of radium per year. This is in very close agreement with the calculated rate (158 cu. mm.). Other experiments not described showed that helium is produced from polonium. F. S.

The Accumulation of Helium in Geological Time. III. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, *A*, **83**, 298—301. Compare this vol., ii, 9).—The ratio of helium to uranium and thorium has been determined for zircons extracted from fourteen rocks ranging from Tertiary to Archean. Minerals like zircon and sphene contain hundreds of times as much helium as the average of the rock of which they are constituents, and accordingly the whole of the contained helium may be regarded as having been generated since the consolida-

tion of the rock and the separation of the mineral. The zircons were decomposed by fusion with borax in a platinum boat in a quartz tube filled with oxygen. The oxygen was removed from the extracted gas by phosphorus, leaving the helium. Each unit in the helium ratio (c.c. per gram of "total equivalent uranium oxide," 1 gram of thoria being reckoned equivalent in helium producing power to 0·203 gram of uranium oxide) is provisionally taken to indicate a period of eleven million years. The helium ratio of zircon stands in very close relation to the geological age of the specimen. For four specimens of the tertiary rocks the ratio is below unity, whilst for four specimens of paleozoic rocks the ratio is between 13 and 29. The oldest specimen from the archæan rocks of Canada has a helium ratio 56·6. These ratios fix the minimum values of the geological age, but in spite of the enormous lengths of time indicated it may be that the whole of the helium generated is not retained. The fraction retained, depending on the structure of the zircon, must be supposed, however, to be fairly definite, and similar for all. F. S.

Rate of Evolution of Heat by Pitchblende. HORACE H. POOLE (*Phil. Mag.*, 1910, [vi], **19**, 314—326).—About half a kilogram of carefully dried powdered Joachimsthal pitchblende, containing 64% of uranium, was placed in a spherical Dewar vessel surrounded with ice, and, when a steady thermal state had been attained, the constant difference of temperature between the under-surface layer of the pitchblende at the bottom of the vessel and the ice outside was determined by means of thermocouples. The heat evolved per hour by the pitchblende was reckoned as the product of this constant difference and the thermal conductance of the calorimeter. The last, which was separately determined with water in the calorimeter, is the number of calories escaping from the calorimeter per hour when the inside is 1° hotter than the outside. To avoid chemical action, of which indications were obtained in the preliminary experiments in air, the calorimeter was filled with carefully dried nitrogen. The conclusion is drawn that 1 gram of the pitchblende evolved $6·1 \times 10^{-5}$ calories per hour as a mean value of three experiments, the separate results being 7·1, 5·45, and 5·85 ($\times 10^{-5}$). The value is surprisingly high, the value calculated, presumably from the kinetic energy of the various α-particles expelled, being only about $4·4 \times 10^{-5}$ for the sample of pitchblende employed. F. S.

The Emission of Positive Rays from Heated Phosphorus Compounds. FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1909, **15**, 329).—The object of the experiments was to test whether the large positive ionisation produced by heated phosphates, notably aluminium phosphate, observed by Sir J. J. Thomson had any connexion with the "anode rays" of Gehrcke and Reichenheim (Abstr., 1908, ii, 343). The latter found most suitable the halide salts of the alkali and alkaline-earth metals, whereas the positive ionisation produced from these when heated is not nearly as great as from the phosphates. The salt, mixed with graphite to make it conduct, and sometimes with silver chloride to fuse the mass together, was rammed into a quartz tube and

strongly heated. The prepared tube was then mounted as anode with another electrode as cathode in an exhausted flask, and a discharge from a large coil passed. No "anode-rays" of the kind obtained from the halides of the alkali metals were obtained from the phosphates, but calcium phosphide and silver chloride did give such rays, the spectrum of their light showing the calcium and silver lines respectively. There is probably no connexion between the two phenomena in question. The experiments support Gehrcke and Reichenheim's conclusions that the "anode rays" owe their origin to the electrolytic decomposition of the salt and expulsion of the metal from the anode into the vacuum. F. S.

Electrical Conductivity and Constitution of Dissolved Substances. S. W. SERKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1—14 [Physical Part]. Compare Abstr., 1909, ii, 372).—According to the solvate theory (compare Jones, Abstr., 1909, ii, 221), a compound like lithium nitrate containing the ion Li, which undergoes intense hydration, should exhibit a well-marked maximum conductivity in mixtures of acetone with an alcohol, whilst potassium iodide should show no trace of a maximum conductivity. The author's conductivity curves are not in agreement with these conclusions. It is found, indeed, that potassium, sodium, and lithium iodides, which differ considerably in the extent of hydration which they undergo, show no maximum conductivity, whilst lithium bromide exhibits a maximum which is not very clearly marked, and lithium chloride a distinct maximum. Neither is there any parallelism observable between the sharpness of this maximum and the magnitude of μ_∞ calculated by the ordinary method of extrapolation. Thus, for lithium chloride, $\mu_\infty = 63$, for lithium iodide $\mu_\infty = 181{\cdot}0$, and for lithium bromide, $\mu_\infty = 144$. The influence of the formation of complex compounds on the molecular conductivity is discussed, and it is found that all the abnormal conductivity curves, corrected for the formation of complex compounds, exhibit characters determined by the corresponding fluidity curves. T. H. P.

Electrical Conductivity of Soap Solutions. JAMES W. McBAIN and MILLICENT TAYLOR (*Ber.*, 1910, **43**, 321—322).—A preliminary account of measurements of the conductivity of solutions of sodium palmitate. The measurements were made in silver vessels, with the following results:

Dilution in litres.............	1	1⅓	2	5	10	20	100
Mol. conductivity in mhos...	64·82	71·13	77·42	77·47	78·77	86·04	135·3

The results are compared with the conductivities of solutions of sodium hydroxide and sodium acetate, and show that the normal soaps do not exist as colloids in concentrated solution. T. S. P.

Diminution of Conductivity by Colloids and Observations relating to the Conductivity of Serum. WALTER FREI (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 94—103).—The influence of serum-albumin, serum-globulin, gelatin, and saponin on the electrical

conductivity of a 0·5*N*-solution of sodium hydroxide at 37° has been examined. For 1% solutions of the four colloids, the conductivity is diminished to the extent of 7 5, 6·6, 5·5, and 5·6% respectively. The specific influence of a given colloid varies somewhat with the concentration. When the conductivity is plotted as a function of the concentration of the colloid, curves are obtained which are slightly convex towards the origin.

It is shown that the observed effects are in part due to phenomena of swelling and adsorption, which cause alterations in the concentration of the dissolved ions. In addition, the conductivity is diminished in consequence of a reduction of the cross-sectional area of the electrolytic solution by the colloidal particles, and also of the increase in the viscosity.

The simultaneous changes observed in the conductivity, freezing-point depression, viscosity, and density on dilution of solutions of serum are interpreted on the basis of the above considerations.

H. M. D.

Dielectric Cohesion of Neon. EDMOND BOUTY (*Compt. rend.*, 1910, **150**, 149—150. Compare Abstr., 1904, ii, 309, 604).—The author has shown previously that the dielectric cohesions of the monatomic gases, helium, argon, and mercury vapour, are considerably less than those of polyatomic gases of comparable molecular weight. The dielectric cohesion of neon, obtained by fractionation of a gaseous mixture of neon, helium, and traces of air, is found to be 7·6, that of air being 435. It is considerably less than that of helium (18·3), although its value would be expected to lie between those of helium and argon. This is in agreement with the fact that Mendeléeff, in his last periodic table, places neon in a separate group from the other rare gases.

Attention is called to luminous effects observed when the pressure on neon is diminished by means of a mercury pump. T. S. P.

Thermodynamics of Standard Cells. ERNST COHEN and HUGO R. KRUYT (*Chem. Weekblad*, 1910, **7**, 69—78).—A criticism of Hulett's calculation of the chemical energy of the Weston standard cell (*Trans. Amer. Electrochem. Soc.*, 1909, **15**, 435). A. J. W.

Electrochemical Equivalent of Silver. F. LAPORTE and P. DE LA GORCE (*Compt. rend.*, 1910, **150**, 278—280).—Improvements introduced into the purification of silver nitrate have brought the authors' earlier results into better agreement with those obtained at the National Physical Laboratory and elsewhere. Crystallisation of the salt between 30° and 40°, under reduced pressure and in the absence of air, gave, as a mean of eight experiments, 1·11827 mg. per Coulomb as the electrochemical equivalent of silver. As a mean between this and other results, the authors adopt 1·11829 mg. as correct. It is important that the air to which the solutions of silver nitrate are exposed should be free from impurities. In one experiment in which tobacco smoke was present, a high result was obtained.

W. O. W.

Correction for the Method of Determining Galvanic Ennobling of Metals. CHARLES M. VAN DEVENTER and H. J. VAN LUMMEL (*Zeitsch. physikal. Chem.*, 1910, **71**, 117—127).—In connexion with the experiments on the galvanic ennobling of metals already described (compare Abstr., 1908, ii, 12, 558; 1909, ii, 958), it has been found necessary to apply a correction for the alteration of the surfaces of the metals during the experiment. This has been done by comparing the potentials of the two metals in acid before and after the "ennobling" experiment. The application of this correction does not greatly alter the results already given. Thus as regards cadmium, lead, tin, nickel, and amalgamated zinc, one electrode can be ennobled with regard to another of the same metal, and for the following pairs of metals, zinc–cadmium, tin–lead, zinc–tin, cadmium–tin, and lead–nickel, the first metal can readily be ennobled with reference to the other. G. S.

Electrolysis of Molten Salts. RICHARD LORENZ (*Festschrift Otto Wallach*, 1909, 513—539).—An account is given of the chief results obtained in recent investigations on the electrolysis of molten salts. The possibility of explaining the observed facts in terms of the theory of electrolytic dissociation is discussed. H. M. D.

Magnetisable Alloys of Manganese. FRIEDRICH HEUSLER (*Festschrift Otto Wallach*, 1909, 467—477. Compare Abstr., 1909, ii, 541).—Polemical against Wedekind. A summary is given of the chief results of work already published in connexion with the magnetic properties of manganese-copper-aluminium alloys.
H. M. D.

Magnetic Measurements of Platinum Metals and of Monoclinic Crystals, in Particular of Iron, Cobalt, and Nickel Salts. WILHELM FINKE (*Ann. Physik*, 1910, [iv], **31**, 149—168).—Measurements have been made of the magnetic susceptibility of platinum, palladium, iridium, and rhodium, and also of ferrous sulphate, nickel sulphate, cobalt sulphate, ferrous ammonium sulphate, nickel ammonium sulphate, cobalt ammonium sulphate, cobalt potassium sulphate, cobalt copper sulphate, epidote, augite, hornblende, adularia, and sucrose.

For the isotropic metals, the susceptibilities are: platinum, $+22{\cdot}6\times10^{-6}$; palladium, $+66{\cdot}26\times10^{-6}$; iridium, $+4{\cdot}89\times10^{-6}$; rhodium, $+12{\cdot}58\times10^{-6}$. In the case of the monoclinic crystals no connexion could be traced between the position of the magnetic axes on the one hand and that of the optic and di-electric axes on the other. H. M. D.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. IV. PAUL PASCAL (*Bull. Soc. chim.*, 1910, [iv], **7**, 45—51. Compare Abstr., 1909, ii, 487, 788, 859, and this vol., ii, 100).—In this paper the anomalous magnetic susceptibilities shown by halogenated and cyano-compounds are considered, and it is shown that the apparent departure from the simple

additive character of this constant is due in the case of haloid derivatives to (1) mutual action of a hydrogen and a halogen atom, and (2) mutual action of halogen atoms, and in the case of cyano-derivatives to the acid character conferred by the cyano-group.

In the case of simple alkyl haloids, the diamagnetic deficit for the whole molecule amounts to about 32×10^{-7} for monochloro-derivatives and to $42 \cdot 5 \times 10^{-7}$ for monobromo- and monoiodo-compounds. For symmetrical dichlorides, it is about 45×10^{-7}, and for dibromides about 60×10^{-7}. Where the two chlorine atoms are attached to the same carbon atom, the deficit is about 67×10^{-7} in open-chain compounds, but it is less where the carbon is attached to a benzene nucleus, thus for $CHPhCl_2$ it is $42 \cdot 5 \times 10^{-7}$.

In cyano-compounds the diamagnetic excess is about 45×10^{-7} for benzonitrile, phenylacetonitrile, or ethyl cyanoacetate, and is of about the same order as in the mineral acids. T. A. H.

Conduction of Heat through Rarefied Gases. Frederick Soddy and Arthur J. Berry (*Proc. Roy. Soc.*, 1910, *A*, 83, 254—264).—The heat dissipated from a bright platinum strip maintained by a current at 61° in various gases has been measured by an electric method at various pressures down to a thermally perfect vacuum. The process of producing high vacua by means of the vapour of calcium was employed. At pressures such that the actual path of the gas molecule is comparable with its mean free path, the heat dissipated is proportional to the pressure of the gas. The conductivity under these conditions bears no relation to the ordinary conductivity at higher pressures, where the conductivity is independent of pressure. The conductivity of acetylene, methane, and cyanogen slightly exceeds that of hydrogen, whilst helium conducts but slightly better than carbon dioxide. In the table, the second column represents the ordinary conductivity of the gases as expressed by the watts dissipated by a definite portion of the strip at pressures above which the conductivity does not further increase with pressure. The third column (K) indicates the found values of the conductivity at low pressure, expressed as the calories ($\times 10^{-5}$) dissipated per cm.² of surface, per 0·01 mm. pressure per 1° difference of temperature. The fourth column (Q) is the value for this conductivity calculated from the kinetic theory on the assumption that the heat interchange at impact is perfect. The last column shows the ratio of K to Q.

	Watts.	*K*.	*Q*.	*K/Q*.
Argon	1·07	1·30	1·20	1·09
Neon	2·35	1·76	1·70	1·04
Carbon dioxide	0·95	1·89	2·64	0·72
Oxygen	1·55	1·91	2·23	0·86
Helium	7·30	1·94	3·80	0·51
Carbon monoxide	1·37	1·96	2·38	0·82
Nitrous oxide	0·97	2·11	2·75	0·77
Nitrogen	1·44	2·21	2·35	0·94
Hydrogen	8·75	2·29	8·95	0·25
Cyanogen	0·97	2·35	—	—
Methane	2·81	2·70	3·95	0·68
Acetylene	1·24	2·75	3·82	0·72

The results indicate a method of obtaining information concerning the nature of the single impact of a molecule on a surface. The interchange of energy appears perfect for the denser monatomic gases, but for the more rapidly moving molecules of helium and hydrogen this is far from the case. In such cases at low temperatures, or for hydrogen if a palladium instead of a platinum surface were used, the conductivity ought to be increased, owing to more perfect interchange of energy on impact. F. S.

Heat Capacity of Certain Metals and Compounds of Metals. HERMANN SCHIMPFF (*Zeitsch. physikal. Chem.*, 1910, **71**, 257—299).—The specific heats of fifteen metals and twenty-nine binary compounds of metals have been determined by the method of mixtures for the three temperature intervals 17 to 100°, 17 to −79°, and 17 to −190°. As the metallic compounds were mainly prepared in the course of the investigations on alloys by Tammann and his pupils, they may be regarded as of well-defined composition. From the results, the mean specific heats at +50°, 0°, −50°, −100°, and −150° are calculated, and are given in tabular form. The limit of experimental error is about 1%.

The mean specific heats of the metals for the three temperature intervals 17 to 100°, 17 to −79°, and 17 to −190° are as follows: Magnesium, 0·2475, 0·2284, 0·2046; aluminium, 0·2173, 0·1976, 0·1696; silicon, 0·1753, 0·1470, 0·1166; chromium, 0·1102, 0 0980, 0·0805; iron, 0·1098 (17 to 100° only); nickel, 0·1088, 0·0974, 0·0830; cobalt, 0·1030, 0·0942, 0·0818; copper, 0·0925, 0·0880, 0 0786; zinc, 0·0934, 0·0886, 0·0819; silver, 0·0560, 0·0544, 0·0506; tin, 0·0556, 0·0521, 0·0488; antimony, 0·0503, 0·0482, 0·0450; gold, 0·0310, 0·0297, 0·0283; platinum, 0·0310, 0·0292, 0·0286; bismuth, 0·0303, 0·0285, 0·0275. The results are compared in detail with those of previous observers, and in the majority of cases the agreement is satisfactory.

For about half the compounds, the specific heats are equal to the sum of the specific heats of the component metals with a maximum deviation of 2%; in the other cases the deviations from Kopp's rule are, in general, within 4%. It is remarkable that in all cases the observed specific heats of the magnesium compounds are smaller, and in most cases those of the antimony compounds greater, than the values calculated according to Kopp's rule.

A formula with three constants is suggested to represent the variation of the specific heats with the temperature between +50° and −150°, and the respective constants for each metal and compound are calculated from the above observations. In all cases the specific heat increases with the temperature, but, except for bismuth and lead, the magnitude of the temperature-coefficient diminishes as the temperature rises. The observations afford no definite information as to the variation of the specific heats above +50° and below −150°.

As regards the atomic heats of the free metals, the average values, excluding silicon, are 4 56, 5·13, 5·60, 5·93, and 6·13 at −150°, −100°, −60°, 0°, and 50°, and the mean values for the metals in combination are 4·24, 4·89, 5·40, 5·75, 5·95 at the same temperatures. G. S.

Specific Heat of Metallic Alloys. ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1708—1711).—In order to test Regnault's law, according to which the specific heat of an alloy is equal to the mean arithmetic specific heat of its components (*Ann. Chim. Phys.*, 1841, [iii], 1, 129), the author has determined the specific heats at 15—100° of alloys of various compositions of (1) bismuth and cadmium, which form neither compounds nor solid solutions; (2) lead and tin, which do not give compounds and only form solid solutions of low concentrations; (3) bismuth and antimony, which form an uninterrupted series of solid solutions; and (4) zinc and antimony, which form the two compounds SbZn and Sb_2Zn_3. In all cases, Regnault's law is confirmed within the limits of experimental error, so that the specific heat of an alloy is an additive property.

T. H. P.

Melting-Point Determinations at Low Temperatures. H. STOLTZENBERG (*Chem. Zeit.*, 1910, **34**, 66—67).—The author describes a modification of his melting-point apparatus for low temperatures (this vol., ii, 17). The tube into which the thermometer dips is double walled, the space between the walls being evacuated.

T. S. P.

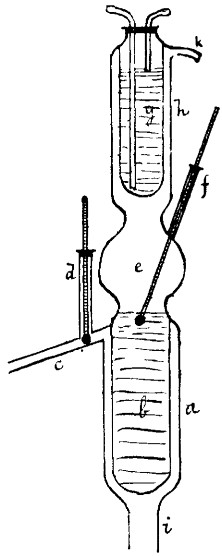
Measurement of the Heats of Liquefaction of Acetic Acid, Benzene, and Nitrobenzene. JULIUS MEYER (*Festschrift Otto Wallach*, 1909, 540—568).—The author has measured the thermal and volume changes which accompany the liquefaction of benzene, nitrobenzene, and acetic acid. Both series of measurements were made with apparatus resembling the Bunsen ice calorimeter. The mean values obtained for the heats of liquefaction are benzene 30·39, nitrobenzene 22·53, acetic acid 45·96 cal. From these data and the observed melting points (5·44°, 5·82°, and 16·54°), the respective molecular freezing-point lowerings are found to be 5·059, 6·849, and 3·621.

The increments of volume on liquefaction of one gram of substance amount to 0·1333, 0·0808, and 0·1578 c.c. respectively. From these data the influence of pressure on the melting point is calculated. The rise of temperature per atmosphere pressure amounts to 0·0295°, 0·0242°, and 0 0241° for benzene, nitrobenzene, and acetic acid respectively, and in all cases these values are found to be in satisfactory agreement with the experimental determinations. H. M. D.

Chloroacetic Acid as a Cryoscopic Solvent. EFISIO MAMELI (*Gazzetta*, 1909, **39**, ii, 579—586).—Of the various modifications of chloroacetic acid, only the most stable or α-form gives good results as a cryoscopic solvent (compare Tanatar, Abstr., 1893, i, 624; Hulett, Abstr., 1899, ii, 468). The mean of the results obtained with xylene, *m*-cresol, safrole, and acetic acid in concentrations not greater than 3% gives the value 52 for the cryoscopic constant of chloroacetic acid, the number calculated by means of van't Hoff's formula being 54·19. Neither the α- nor β-modification of chloroacetic acid forms solid solutions with acetic acid, both giving normal molecular weights in this solvent.

The molecular weight of water in freezing chloroacetic acid is slightly above the normal value at low concentrations, and about 1·5 times the calculated value for a 12% solution. With phosphoryl chloride the molecular weight is less than the normal at low concentrations and increases with the concentration, the calculated value being passed at about 1·3%.

With aniline, pyridine, and quinoline, chloroacetic acid behaves as a slightly dissociating solvent, the molecular weights being somewhat lower than the normal values, even for very dilute solutions, and decreasing gradully as the concentration increases. T. H. P.



A New Fractionating Column. ALFRED HAHN (*Ber.*, 1910, **43**, 419—423).—The principle of the column is that the vapour from the boiling liquid passes through a space which is kept at a constant temperature, but, nevertheless, can absorb heat readily. The details of the apparatus will be readily understood from the diagram. The constant temperature in the narrow space, *a*, through which the vapour of the boiling liquid passes, is maintained by the boiling liquid in *b*. This latter liquid must be chosen to give a suitable temperature, and its boiling point may be altered by connecting *k* with a water pump; *g* is a condenser for the liquid boiling in *b*.

With this apparatus the distillate from a 45% alcohol consisted of 96% alcohol, the liquid in *b* being at 76°; other fractionating columns gave a 92—93% distillate. Mixtures of ether and alcohol, methyl and ethyl alcohols, and of methyl ethyl ketone (b. p. 81°) and diacetyl (b. p. 87°) were satisfactorily separated.

The apparatus possesses the great advantage that it does not require continual watching. T. S. P.

An Apparatus for the Measurement of the Vapour Pressures of Dilute Aqueous Solutions. RUDOLF MAIER (*Ann. Physik*, 1910, [iv], **31**, 423—435).—An apparatus has been devised by means of which the small differences between the vapour pressures of water and dilute aqueous solutions can be measured with considerable accuracy. The arrangement is such that absolute measurements of small vapour pressures can also be made.

The mercury manometer consists of a U-shaped tube, supported firmly on a stand provided with levelling screws. A fine platinum-iridium point is supported in each arm of the tube, and contact of these with the mercury is indicated electrically. Each of the supports, to which the platinium-iridium needles are attached, is capable of vertical movement, the amount of which is measured by means of a micrometer screw.

Another essential feature of the apparatus is the special arrangement adopted for ensuring that the two liquids shall have the same temperature. This consists of a double vessel, the inner and outer parts of which are connected with tubes leading to the manometer by carefully ground glass joints. The inner vessel, in which the water is placed, is of platinum, which facilitates the attainment of thermal equilibrium between its contents and the solution which surrounds it.

The data obtained in experiments with solutions of sucrose in water at 0° are recorded. The vapour-pressure differences thus found are in good agreement with those calculated from Raoult's vapour-pressure equation.

H. M. D.

Partial Pressures of Liquid Mixtures. WILLIAM E. STORY (*Zeitsch. physikal. Chem.*, 1909, 71, 129—151).—A mathematical paper. The Duhem-Margules equation, which refers to the vapour pressures of the components of a binary mixture, has been extended to mixtures with any number of components, and a general solution of the equation is given. It is shown that Raoult's law can be deduced directly from the Duhem-Margules formula, and that the latter formula is based on no other assumptions than those comprised in Raoult's law. The series containing the solution of the equation are more convergent than those hitherto used. The methods of deducing the coefficients of the formulæ from the experimental data are discussed in detail.

G. S.

Binary Mixtures and Concentrated Solutions. II. FRIEDRICH DOLEZALEK (*Zeitsch. physikal. Chem.*, 1910, 71, 191—213. Compare Abstr., 1909, ii, 22; Bein, *ibid.*, 471; Möller, *ibid.*, 981).—The theory of the vapour-pressure of binary mixtures described in the previous paper is illustrated by further examples, and is extended to other properties of these mixtures.

From the total vapour-pressure curve of mixtures of ethyl ether and chloroform, as determined by Guthrie (Abstr., 1885, 339), the partial vapour-pressure curves of the components are deduced, and it is shown that the components enter into combination in molecular proportions. At 19°, when the components are present in equimolar proportions, the mixture contains 24 mol. % of the compound. The view that a compound containing one molecule of each of the components is formed is further supported by the fact that the heat of admixture, and the contraction on mixing, both attain a maximum value when the components are present in equivalent proportions.

Similarly, from the determination by Inglis (Abstr., 1906, ii, 332) of the partial pressures of nitrogen and oxygen above mixtures of the liquefied gases, it is shown that liquid nitrogen is non-associated and liquid oxygen associated. At 74·7° abs., in a mixture of liquefied oxygen and nitrogen in molar proportions, there is about 1 mol. O_4 for every 7 mols. O_2, and in pure oxygen 1 mol. O_4 for 3·03 mols. O_2. At 79·07° there is 1 mol. O_4 for 4·53 mols. O_2, and above 86° abs. oxygen exists only as simple molecules.

The application of the theory to the solubility of a gas in a liquid, on the assumption that the system is a highly concentrated solution of

the liquid in the liquefied gas, leads to the expression : $p/p_0 = q$, where p is the partial pressure of the gas, and p_0 is the vapour pressure of the liquefied gas (in the unimolecular form) at the same temperature. Hence, if the same gas is dissolved at the same pressure and temperature in different liquids, p and p_0, and, therefore, q, have the same values throughout; the solubility of a gas, expressed as a true molar fraction, should be the same for all chemically indifferent liquids. This deduction is shown to be approximately valid for the solubility of carbon dioxide in benzene, chlorobenzene, bromobenzene, and chloroform when for p_0 the corrected pressure $p_0 + a/v^2$, in the sense of van der Waals, is used. The applicability of the method is limited by the fact that at the temperatures at which solubilities are usually measured, the permanent gases are far above their respective critical temperatures.

Further, the theory leads to the result that the ratio of the solubilities of two indifferent gases should be the same for different solvents, provided that the molecular weights of the solvents are not greatly affected by dissolving the gases in them. This law has already been discovered experimentally by Just (Abstr., 1901, ii, 439).

The expansion of a liquid produced by dissolving a gas in it has also been calculated, and the observed and calculated values are in good agreement. Finally, the thermal phenomena observed on admixture of liquids are also satisfactorily represented by the theory. G. S.

Experimental Determination and Thermodynamic Calculation of the Vapour Pressures of Toluene, Naphthalene, and Benzene. JONATHAN T. BARKER (*Zeitsch. physikal. Chem.*, 1910, **71**, 235—253).—The vapour pressures of toluene through a wide range of temperature, of liquid and solid naphthalene, and of solid benzene have been determined by the dynamical method, a current of oxygen being saturated with the organic vapour, and the amount of the latter carried over determined by combustion. Various arrangements for securing saturation of the oxygen are described. The method proved satisfactory down to vapour pressures equal to 0·005 mm. of mercury.

The vapour pressures of toluene, in mm. of mercury at 0°, are as follows: 0·0054 at −78°, 1·61 at −21°, 16·8 at 14·8°, 28·75 at 25·8°; of naphthalene, 0·064 at 20°, 0·164 at 30°, and 0·378 at 40°; and of benzene, 0·0180 at −77·5°. Data for these substances at other temperatures are already available.

The object of the determinations was to test the vapour-pressure formula of Nernst: $\log p = -\lambda_0/4{\cdot}571T + 3{\cdot}5/R.\log T - \epsilon T/4{\cdot}571 + C$, where λ_0, ϵ, and C are constants related in a definite way to the properties of the substance. The formula represents the experimental results satisfactorily. The calculated molecular heat of vaporisation of toluene at 111° is 7775 cal. as compared with the experimental values 7687 cal. (Schiff) and 8044 cal. (Campbell Brown). The latent heat of fusion of naphthalene (calculated) is 4435 cal. per mol., in good agreement with the experimental value. The calculated heat of vaporisation of solid benzene is 10,220 cal. per mol.; it has not been determined directly. The calculated heat of fusion of benzene,

1900 cal. per mol., does not agree very satisfactorily with the mean of the experimental values, 2326 cal. G. S.

Corresponding States. KIRSTINE MEYER *née* BJERRUM (*Zeitsch. physikal. Chem.*, 1910, **71**, 325—336).—In a previous paper (Abstr., 1900, ii, 263) it was pointed out that van der Waals' theory of corresponding states is not strictly applicable, but that a good agreement between theory and experiment is observed when for each substance a special minimum temperature and minimum volume is calculated, and different units of pressure, volume, and temperature are used. In this way a common vapour-pressure curve for twenty-five substances has been obtained with the ordinate $y=(P_c-P)/P_c$ and abscissa $x=(T_c-T)/K$, where K is a temperature constant and the other symbols have the usual significance. It is now shown, mainly by means of data due to Young, that octane, di*iso*propyl, di*iso*butyl, and hexamethylene, as well as chlorine and carbon dioxide, follow the law fairly accurately.

In the former paper, T_{min} was taken as zero for fluorbenzene, and other substances were referred to this arbitrary value. In order to give K a more definite meaning, hydrogen is now chosen as reference substance, so that K represents the difference between the critical temperature of the substance T_c and the lowest temperature, T_{min}, at which the substance can exist in the gaseous condition, the assumption being made that this is true for hydrogen in the neighbourhood of the absolute zero. On this basis it is shown, from the data of Ramsay, Travers, Olszewski, and others, that nitrogen and the gases of the argon series follow the law, and the values of $T_{min}=T_c-K$ are calculated for a large number of substances.

When helium is chosen as the reference substance, for which T_{min} is zero, T_{min} for hydrogen becomes 7·9, but the values for T_{min} calculated on this basis for other substances are too high, a result due to the uncertainty as to the critical temperature and other data for helium.

G. S.

Laws of Evaporation. PIERRE VAILLANT (*Compt. rend.*, 1910, **150**, 213—216. Compare Abstr., 1908, ii, 460; 1909, ii, 544).—The supposition has been advanced that the rate of evaporation of an aqueous solution depends solely on the rate of diffusion of aqueous vapour out of a layer of saturated air in the immediate neighbourhood of the surface. This is supported by the observation that when the solution is contained in a vessel with an opening of known area, the quantity of liquid evaporated per second (Q) is not proportional to S, the area of the opening, but is a function of S independent of the nature of the liquid. It has also been shown, that in the case of an incompletely filled, straight-walled vessel, the speed of evaporation is governed by the formula $Q=aMF^{4/3}$, where M denotes the molecular weight of the liquid and F its vapour tension, whilst a is a constant almost independent of the nature of the liquid. Eighteen liquids have been studied, including water, carbon disulphide, hydrocarbons, alcohols, ethers, and organic halogen derivatives; the results are given in tabular form. W. O. W.

Thermochemical Investigations of Organic Compounds. IV—VII. Sulphur, Halogen, and Unsaturated Compounds. W. ŚWIĘTOSŁAWSKI [SVENTOSLAVSKY] (*Bull. Acad. Sci. Cracow*, 1909, 941—972. Compare Abstr., 1909, ii, 23, 213, 547).—The analysis of thermochemical data is extended to compounds containing sulphur and the halogens and to unsaturated compounds.

From the data for mercaptans and sulphides, the conclusion is drawn that the heat of formation of the linking C–S is greater in the sulphides than in the corresponding mercaptans. This result is the same as that found in the case of ethers and the corresponding alcohols.

Although the data for halogen compounds have not been accurately determined, the numbers obtained by different observers exhibiting considerable divergence, the heats of formation of the linkings C–Cl, C–Br, and C–I appear to be regulated by the same laws as those which govern the heat quantities associated with the linkings between carbon and other univalent groups.

From the data for unsaturated compounds, the conclusion is drawn that the minimum value of the heat of formation of the linking C–C is about 18·0 Cal.

By means of the equations which express the thermochemical values of the linkings between carbon and other elements and between hydrogen and other elements, the heat changes corresponding with the equation (C–X) + (H–Y) = (C–Y) + (H–X) are calculated, X and Y representing any of the elements: carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, bromine, and iodine. H. M. D.

Andrews' Measurements of the Compression of Carbon Dioxide and of Mixtures of Carbon Dioxide and Nitrogen. C. G. KNOTT (*Proc. Roy. Soc. Edin.*, 1909, **30**, 1—22).—The data obtained by Andrews in his classical experiments on the compressibility of carbon dioxide are tabulated in compact form. Similar data are also recorded for mixtures containing nitrogen and carbon dioxide in the volume ratios 1 : 3·43 and 1 : 6·2. These data have been collected partly from the memoirs published in 1869, 1876, and 1886, and partly from note-books left by Andrews. H. M. D.

Dependence of the Cubic Compressibility of Potassium and Sodium on the Temperature. LUDWIG PROTZ (*Ann. Physik*, 1910, [iv], **31**, 127—148).—By means of thermodynamic reasoning it can be shown that the difference between the specific heats of a substance at constant pressure and at constant volume is dependent on the compressibility of the substance. With the object of obtaining information in regard to the variation of this difference with the temperature, the author has measured the compressibility of potassium and sodium at different temperatures.

The piezometric arrangement used in the experiments was similar to that described by Röntgen and Schneider. Measurements of the compressibility of water and petroleum were made in the first instance, the data for water being utilised in the calibration of the apparatus,

and those for petroleum in connexion with the compressibility of the solid metals. The experimental results show that the compressibility of potassium, sodium, and petroleum increases with the temperature according to a linear equation. From this it follows that the difference between the two specific heats increases with the temperature in the case of the two alkali metals.

In the case of water, a minimum compressibility is found at about 60°. H. M. D.

Condensation of Water by Electrolytes. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1910, **14**, 1—11).—The densities of solutions of certain acids, bases, and salts, in concentrations varying from $N/10$ to $N/200$, have been carefully determined at 25° by a pyknometer method, and from the results the amount of water "condensed" by a mol. of each electrolyte has been calculated on the assumption that the latter retains its volume in the anhydrous form unchanged in solution. The results do not show any very definite regularities. Substances which show large heats of solution or have a tendency to crystallise with water of crystallisation have relatively high condensing power. The specific condensing power usually diminishes with increased concentration, but for hydrochloric and nitric acids the condensation increases at first with the concentration, attains a maximum in approximately 1% solution, and beyond that point diminishes. The results of previous observers on this subject are summarised. G. S.

A Method of Determining the Viscosity of Gases, especially those available only in Small Quantities. A. O. RANKINE (*Proc. Roy. Soc.*, 1910, *A*, **83**, 265—276).—The apparatus, which has been designed for measurements of viscosity with small quantities of gases, consists of two parallel tubes connected at both ends. One of the tubes consists of a very fine capillary, the other being of much greater cross-sectional area, yet sufficiently narrow for a pellet of mercury to remain intact inside it. Taps are provided above and below for the purpose of cleaning the tubes and filling the apparatus with gas. The rate of fall of the mercury pellet in the wider tube is determined by the viscosity of the gas which is forced through the capillary tube as the mercury descends. The formula from which the viscosity is calculated is $\eta = \pi R^4 pt/8lv$, in which R is the radius of the capillary tube, l its length, p the difference of pressure on the two sides of the mercury, v the volume of gas forced through the capillary, and t the time of fall. On account of capillary attraction, the value of p is not proportional to the length of the pellet of mercury, but it is shown that the capillary effect can be eliminated by using different lengths of mercury.

The apparatus was used for determining the viscosity of dry air at different temperatures. The absolute values at 11·2°, 15·5°, and 19·2° are respectively 1·770, 1·803, and $1{\cdot}828 \times 10^{-4}$.

It is proposed to use the apparatus for the examination of neon, xenon, and krypton. For observations at high pressures, the method

described is much simpler than those which have been previously used. On the other hand, it is not suitable for work at low pressures.

H. M. D.

Torsional Elasticity and its Connection with Viscosity. O. FAUST and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1910, **71**, 51—58. Compare Lauer and Tammann, Abstr., 1908, ii, 667).—The elasticity measurements were made by the method already described (*loc. cit.*); the viscosity measurements were taken from available data, and in a few cases were made by the usual time of flow method. Data for twenty-five liquids are given. For liquids of high viscosity there was only one back movement after the impulse and then a slow movement to the null position; for those of smaller viscosity unsymmetrical swinging about the null position; both phenomena indicate the existence of torsional elasticity. For those with still less viscosity, the swinging was symmetrical about the null position, indicating absence of torsional elasticity.

Viscosity and torsional elasticity are directly proportional. For all substances with a viscosity less than $4 \cdot 3 \times 10^{-2}$, no torsional elasticity was observed under the experimental conditions, but all substances with a viscosity greater than $8 \cdot 6 \times 10^{-2}$ showed the above property. The ratio of the single backward movement to the movement produced by the impulse increases with the viscosity, and even exceeds unity for liquids of the highest viscosity. The magnitude of the viscosity at which torsional elasticity becomes marked depends on the sensitiveness of the measuring apparatus.

The proportionality between viscosity and elasticity has also been shown by allowing certain liquids to cool slowly and determining the viscosity at which torsional elasticity can just be detected by a very sensitive method. In all cases it appears at approximately the same value of the viscosity.

Certain viscous liquids become doubly refracting under stress, and it is shown from the data of previous observers that for castor oil the magnitude of the forced double refraction alters with the temperature proportionally to the viscosity.

G. S.

Absorption of Liquids by Porous Substances. J. H. RUSSENBERGER (*Compt. rend.*, 1910, **150**, 275—278).—The "absorptive power" of a substance may be determined by suspending a thread of the material at one end of a wire passing over a pulley. The thread dips in water, which rises to a height h, and a weight, p, is attached to the other end of the wire to secure equilibrium. The author develops the following expression to represent the absorptive power: $X = \frac{p}{QS} \cdot \frac{dh}{dt} = \frac{h}{Q} \cdot \frac{dh}{dt}$, where S is the area of the cross section of the thread, Q the weight of absorbent material in unit-volume, and dh/dt denotes the speed at which the water rises. It is found by experiment that for the same kind of material, X is approximately constant.

By integretion $h^2 = 2QXt + C$. It is, therefore, only necessary to

measure the height to which water rises in a thread of cotton held between two glass plates, to have a measure of its absorptive power.

W. O. W.

Three-phase Equilibrium (with a Pressure Minimum) of a Dissociating Compound of Two Components. III. Gerard H. Leopold (*Zeitsch. physikal. Chem.*, 1910, **71**, 59—89. Compare Abstr., 1908, ii, 218, 472).—The complete equilibrium between aniline hydrochloride and its components has been investigated.

The m. p. of aniline hydrochloride is 199·2—199·3°, and at this temperature it is only very slightly dissociated. The freezing-point curve of the system aniline–hydrogen chloride has been determined, and no evidence of the existence of a compound other than the above has been obtained.

Within certain narrow limits, aniline hydrochloride and hydrogen chloride are not completely miscible; the lowest temperature at which this occurs is 10·5°, the mixture containing 5·3 mol.% of aniline, and the highest temperature 51·1°, which is the critical temperature of the upper liquid layer and the vapour. This critical temperature is very slightly lower (0·15—0·20°) than that of pure hydrogen chloride.

The mixture of maximum boiling point at atmospheric pressure contains about 51 mol.% aniline. The b. p. of aniline hydrochloride itself cannot be determined in the ordinary way, as part of the hydrogen chloride at once escapes, and the constant boiling mixture is obtained; the boiling point of the latter is 244·4°. The boiling-point curve of mixtures of the constant-boiling liquid and aniline has also been determined.

The boiling-point curve for a lower pressure has also been deduced by construction from the three-phase curve and the melting-point curve; in this case the maximum occurs in a mixture containing 50·8 mol.% of aniline.

The vapour-pressure curve of aniline hydrochloride has been determined. In this case the melting point occurs, as already mentioned, at 199·2°, and a vapour pressure of 19·4 cm., whilst the maximum sublimation point occurs at 198° and a pressure of 16·2 cm.

Finally, the three-phase curves have been determined for mixtures containing excess of aniline and of hydrogen chloride respectively in the liquid phase. In the curve of the former system there is a maximum at 175° and 29·2 cm. pressure, and a minimum at 197 5 and 16·0 cm. pressure. The maximum for mixtures containing excess of hydrogen chloride could not be measured directly, owing to the high pressure, but other parts of the curve have been determined.

G. S.

Relation between Density and Degree of Dissociation of Aqueous Salt Solutions. S. Tereschin (*Ber. Deut. physikal. Ges.*, 1910, **12**, 50—53).—The author has shown previously (Abstr., 1909, ii, 552) that the constant A_s of Heydweiller's formula (*Ber. Deut. physikal. Ges.*, 1909, **11**, 37) may be regarded as the sum of two moduli, each belonging to one of the ions and independent of the nature of the

other ion. By means of Heydweiller's further results (this vol., ii, 106), the author shows that these density moduli are subject to certain laws. Thus, the moduli of the elementary ions increase proportionally to the atomic weight in the separate groups of the periodic system. The magnitude of the water envelope surrounding the ion is doubtless related closely to the density modulus (compare Kohlrausch, Abstr., 1902, ii, 489). Possibly the irregular position occupied by fluorine as regards its mobility and the temperature-coefficient of the latter, in comparison with the other members of the halogen group (Kohlrausch, *loc. cit.*), is to be attributed to the abnormal magnitude of its density modulus, which is considerably higher than it should be according to the straight line curve between the moduli and atomic weights. T. H. P.

Behaviour of Aqueous Solutions in Capillary Actions. ZDENKO H. SKRAUP (*Monatsh.*, 1909, **30**, 773—824).—The present communication contains the results of a large number of observations made with acids, bases, and salts of the most varied character; it is not yet possible to make strictly accurate generalisations, although the statements made previously (Abstr., 1909, ii, 868) receive further support from the results of the extended inquiry. The following are the most striking results not published hitherto: (1) In equivalent and extremely dilute solutions, strong bases ascend higher than strong acids. (2) Phosphoric acid, although a relatively weak acid, does not ascend to the same height as the strongest acids. (3) In general, salts ascend much higher than the acids or bases, in equivalent solutions, of which they are formed; in many cases the salt rises to practically the same height as the water. (4) Sucrose and antipyrine, in all degrees of dilution, ascend to the same height as the water. (5) Colloidal ferric hydroxide, in strong solutions, appears to retard the ascent of water.

Observations, similar to those made with filter paper, have been made with silk, wool, and plates of unglazed porcelain and plaster of Paris. W. H. G.

Diffusion and the Kinetic Theory of Solutions. J. THOVERT (*Compt. rend.*, 1910, **150**, 270—272. Compare Abstr., 1903, ii, 13). —The relation between the molecular weight, M, and the diffusion coefficient, D, of a substance in solution has been represented by the formula $D\sqrt{M}=C$, where C is a constant. For a large number of substances it has been shown that $C=12\times10^{-5}$; it is now found, however, that in many cases C may have a much larger value. Compounds of similar structure usually show the same value for C. An explanation, based on the kinetic theory, is put forward to account for these observations. W. O. W.

Action of Membranes. HEINRICH BECHHOLD and J. ZIEGLER (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 122—123).—The authors object to the view put forward by Liesegang respecting the nature of precipitation membranes. In the case of the membrane which is formed when equimolecular solutions of sodium chloride and silver

nitrate in gelatin are allowed to diffuse towards one another, a condition of statical equilibrium is set up. After the formation of the membrane, no further reaction between the two substances can be observed. H. M. D.

Properties of Solutions at their Critical Solution-Temperatures. A. N. SCHÜKAREFF (*Zeitsch. physikal. Chem.*, 1910, **71**, 90—108. Compare *ibid.*, 1897, **23**, 308).—It is shown that at the critical solution-temperature of two liquids many properties of the solutions follow very simple rules.

It has already been shown (*loc. cit.*) that the internal energy E of mixtures of phenol and water at their critical solution-temperature can be represented as the sum of two factors, thus $E = E_w + nE_{Ph}$, where E_w represents the internal energy of 1 mol. of water, E_{Ph} that of 1 mol. of dissolved phenol, and n the number of mols. of phenol for 1 mol. of water. It is now shown that the same rule holds for mixtures of acetylacetone and water, propionitrile and water, and resorcinol and benzene, but not for propionitrile and an aqueous solution of sodium chloride.

Further, the respective capillary coefficients ($= rsH$, where the symbols have the usual significance) of mixtures of phenol and water and of acetylacetone and water are constants independent of the composition of the solutions at the respective critical solution-temperatures. Similarly, the vapour pressure of certain pairs of liquids with an upper critical solution-temperature is independent of the composition within the limits of 20—80% at the temperature in question, and the vapour pressure of mixtures of nicotine and water is constant between 17 and 82% nicotine at the lower critical solution-temperature. At the upper critical solution-temperature, the vapour pressure of the solutions is generally greater than that of the more volatile component. Finally, the expansion-coefficient of mixtures of acetylacetone and water is approximately constant between 15 and 79% of the former component in the neighbourhood of the critical solution-temperature.

The influence of a number of compounds (acids, salts, and sugars) on the critical solution-temperature of a mixture of propionitrile and water has been determined, but there is no apparent connexion between the magnitude of the elevation and the nature of the third substance. G. S.

An Example of Solubility Influence. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **65**, 341—344).—The solubility of succinic acid in water at 25° is 6·72 millimols. in 10 c.c. This value is much lowered by the addition of alkali salts, the lowering being approximately proportional to the concentration of the salt in the case of potassium chloride, bromide, and iodide, but being greatest in small concentrations for sodium and lithium chlorides.

The reciprocal lowering of the solubility of sodium chloride by succinic acid has also been measured. The formula given by Rothmund and Wilsmore (Abstr., 1902, ii, 447) is not exactly confirmed, owing to the high concentration of the solution.

In the salts examined, the influence increases with diminishing

electro-affinity of the metal, and also, although to a less extent, with increasing electro-affinity of the anion. C. H. D.

Difference in the Speed of Dissolution of Sucrose Crystals at their Different Faces. GASTON GAILLARD (*Compt. rend.*, 1910, **150**, 217—219).—Observations have been made on sucrose by immersing different faces of a crystal in water for a definite time. The area of the crystal face was measured, and the amount of dissolved solid determined polarimetrically. Results are given in tabular form, from which it appears that the speed of dissolution varies somewhat according to the face of the crystal undergoing attack by the solvent. W. O. W.

Crystallisation in Fused Masses, owing to the Liberation of Gas. FRITZ RINNE (*Jahrb. Min.*, 1909, ii, 129—139).—By the evolution of a gaseous product, the composition of a fused mass may be so altered that crystallisation takes place without any fall in temperature. The conditions of equilibrium in such systems are illustrated by diagrams, and the example most fully worked out is the conversion of white cast-iron into wrought-iron by the puddling process. Samples of iron were taken at different stages of the process, the percentage of carbon determined, and sections of the metal examined under the microscope. As the carbon is burnt off, there is a crystallisation of martensite from the fluid metal. In the same way, crystallisation of silver or gold may take place during the cupellation of silver-lead or gold-lead alloys, owing to the distillation or oxidation of the lead. In aqueous solutions of salts, a similar change in composition is effected by the evaporation of the solvent; and in igneous magmas it is possible that crystallisation may also be induced by an alteration in composition accompanying the liberation of volcanic gases. L. J. S.

Spontaneous Crystallisation of Sugar. G. FOUQUET (*Compt. rend.*, 1910, **150**, 280—282).—Observations have been made on the temperature at which spontaneous crystallisation begins in supersaturated sugar solutions submitted to mechanical stirring. As a result, the author confirms the observations of Miers in the case of other substances, that the curve of supersaturation obtained by plotting concentration against the temperature at which crystallisation commences is approximately parallel to the curve of solubility. The addition of impurities does not appear to affect this parallelism. W. O. W.

Liquid Crystals and Avogadro's Hypothesis. OTTO LEHMANN (*Zeitsch. physikal. Chem.*, 1910, **71**, 355—381).—The paper consists largely of references to the author's earlier work on liquid crystals.

The generally accepted view as to the nature of liquid crystals is incompatible with Avogadro's hypothesis, and the author, therefore, considers that the hypothesis in question is not valid. The consequences drawn from it as to the identity of molecular weight in different states of aggregation (including van der Waals' theory of

continuity) cannot be upheld. The existence of a transition temperature for enantiotropic modifications, and of mixed crystals of non-isomorphous modifications, are also regarded as incompatible with Avogadro's hypothesis. The assumption made in deducing Avogadro's hypothesis from the principles of the kinetic theory, that the mass of a molecule is constant, is not applicable to gases and liquids where the molecules can readily combine and decompose.

The views as to the nature of liquid crystals advocated in different editions of Nernst's *Theoretische Chemie* are adversely criticised, and the author contends that his priority in reference to a number of discoveries referring more particularly to crystals has been disregarded by Nernst. G. S.

Self-purification of Liquid Crystals. OTTO LEHMANN (*Physikal. Zeitsch.*, 1910, **11**, 44—49).—Experiments are described which indicate that the formation of liquid crystals from isotropic liquids is accompanied by a purification process analogous to that which attends the separation of solid, crystalline aggregates from isotropic liquids. This can be observed, for instance, when very finely divided and specifically light substances (such as spores of *Lycoperdon*) are added to *p*-azoxyanisole in the isotropic condition, and the temperature is then allowed to fall, so that the anisotropic form of the substance makes its appearance. The observations indicate that, in general, colloidal solutions in crystalline liquids are not obtainable. This is regarded as another argument in favour of the author's theory of the nature of liquid crystals, as against the emulsion theory. H. M. D.

Emulsions. WA. OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 103—109).—In connexion with the technical impregnation of wood with coal-tar oils, the author has investigated the nature of the emulsions which are formed by oils with water. Since both the oil and the water can take the part of the disperse colloid, or of the dispersive medium, it is evident that there are two critical points which determine the limiting concentrations for disperse systems in which the respective substances play the part of dispersive medium. For mixtures of the two substances which fall between these limits, two kinds of emulsions can be obtained which have quite different properties. The character of the emulsion which is formed in any given case is shown to depend on the previous history of the substances. If the carefully cleaned interior surface of the vessel in which the emulsion is prepared has been previously covered with oil, the emulsion obtained is of the one type; if previously covered with water, the second type of emulsion is obtained. The effect of a surface layer of oil is apparently to destroy the colloidal disperse oil particles which may be formed on agitation, and, similarly, the effect of a water surface is to nullify the tendency of the water to distribute itself in the form of a disperse colloidally suspended phase. H. M. D.

Independent Components and Compounds. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1910, **71**, 337—354).—A theoretical paper. The conditions are investigated under which, in a two-phase system,

a system made up of n elements behaves as a system of $n-1$ substances. For a system made up of two elements, these conditions can only be fulfilled in one way, and the simple relation $r_1/s_1 = r_2/s_2$ holds (r_1 and r_2 being the amounts of heat taken up by the system, and s_1 resp. s_2 the changes of volume which occur when unit mass of the first of the second component respectively is transferred at constant temperature and pressure from the first to the second phase), which is equivalent to the law of constant proportions for a binary compound which boils, fuses, or undergoes transition without decomposition. When n exceeds 2, the conditions may be fulfilled in different ways, but the preferable solution leads to an equation of the same form as the above, which therefore applies to a binary system on addition of other elements provided that the compound behaves to these as a whole. G. S.

Allotropy and Internal Equilibrium. ANDREAS SMITS (*Chem. Weekblad*, 1910, **7**, 79—83).—A theoretical paper. A. J. W.

The Equilibrium Solid–Liquid–Gas in Binary Systems which Present Mixed Crystals. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 537—545).—A theoretical paper in which the author discusses the various possible forms of the three-phase equilibrium curves for binary systems in which the two components are completely miscible in the solid state. H. M. D.

Equilibria in Quaternary Systems. The System: Lithum Sulphate–Ammonium Sulphate–Ferrous Sulphate and Water. FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1910, **71**, 109—116).—The three ternary systems and the quaternary system have been investigated by solubility measurements at 30° in the usual way, and the results are represented in two ways on projected space diagrams.

The solid phases in the quaternary system are $(NH_4)_2SO_4$, Li_2SO_4,H_2O, $FeSO_4,7H_2O$, $Li_2SO_4,(NH_4)_2SO_4 = D_{Li}$, and

$$FeSO_4,(NH_4)_2SO_4,6H_2O = D_{Fe}.$$

The results show that $FeSO_4,7H_2O$ can co-exist with Li_2SO_4,H_2O and D_{Fe}, but not with $(NH_4)_2SO_4$ and D_{Li}; that Li_2SO_4,H_2O can co-exist with $FeSO_4,7H_2O$, D_{Fe}, and D_{Li}, but not with $(NH_4)_2SO_4$; that $(NH_4)_2SO_4$ can co-exist with D_{Fe} and D_{Li}, but not with the other two salts; that D_{Li} can co-exist with all the other salts except $FeSO_4,7H_2O$, and, finally, that D_{Fe} can co-exist with all the other solid salts.

G. S.

Criteria for the Determination of the Sensitiveness of Precipitation Reactions. WILHELM BÖTTGER (*Festschrift Otto Wallach*, 1909, 282—300).—Experiments have been made to determine the smallest concentration at which potassium chloride, bromide, and iodate can be detected by the formation of a visible precipitate on the addition of silver nitrate. For this purpose, a definite volume of a solution containing a relatively large excess of silver nitrate was added to measured volumes of solutions of the halogen salts of gradually decreasing concentration. The observations indicate that the limiting concentrations for the chloride, bromide, and iodate are respectively $0{\cdot}16 \times 10^{-5}$, $0{\cdot}04 \times 10^{-5}$, and 1×10^{-5} mol. per litre. In the case of the

precipitation of silver chloride, the limiting concentration falls to $0{\cdot}04 \times 10^{-5}$ mol. per litre in presence of nitric acid. This increase in sensitiveness is attributed to the formation of particles of larger size when nitric acid is present in the solution. On the other hand, there appears to be a limit to the increase in sensitiveness on this account, for the silver iodate is precipitated in the form of well-defined, crystalline particles of relatively large size, and it is to this circumstance that the relative insensitiveness of the visible reaction between iodate and silver nitrate appears to be due.

It is shown that observations of the above nature can be utilised to determine approximately the solubility of slightly soluble substances, provided that these are not especially characterised by the ready formation of supersaturated solutions. H. M. D.

Relationship between the Structure of the Aliphatic Alcohols and their Rate of Esterification. ARTHUR MICHAEL (*Ber.*, 1910, **43**, 464—465. Compare Michael and Wolgast, Abstr., 1909, ii, 873).—Polemical in reply to B. N. Menschutkin (*ibid.*, 988). It is pointed out that the methods used by N. Menschutkin and by Michael and Wolgast are essentially different, and the results are not comparable. J. J. S.

Modification of Dunstan and Short's Extraction Apparatus. P. Ê. F. PERRÉDÈS (*Pharm. J.*, 1910, [iv], **30**, 106).—In using this apparatus in its original form, the contents of the inner tube are liable to be carried into the outer tube of the extractor if the solvent is boiled vigorously. To avoid this, the author inserts a spiral spring of brass wire, provided with a suitable disk of wire gauze at the lower end, and a ring at the other. The lower end rests on the contents of the inner tube, and the other end against the cork with which the extractor is closed. The modified apparatus is figured in the original. T. A. H.

[Lecture] Experiments in Physical Chemistry. UGO GRASSI (*Nuovo Cim.*, 1909, [v], **18**, ii, 408—412).—The author describes suitable apparatus for (1) measuring the catalytic action of hydrochloric acid on the reaction between menthone (or acetophenone) and phenylhydrazine; (2) studying the law of mass action in the dissociation of nitrogen peroxide, and (3) measuring the lowering of solubility in water effected by a substance dissolved in ether. T. H. P.

Inorganic Chemistry.

Formulation and Nomenclature of Inorganic Compounds. MAX K. HOFFMANN (*Chem. Zeit.*, 1910, **34**, 73—76).—A scheme is put forward for the systematic formulation and nomenclature of inorganic compounds. The following points are considered : (1) The sequence

of the elements and radicles in the various compounds. (2) The order in which the various oxidation stages of the same element should be placed in a formula. (3) The naming of numbers, for example, mono-, di-, tri-, etc. (4) The nomenclature of (*a*) individual elements, (*b*) anions, (*c*) alloys, (*d*) metalammines, (*e*) double salts. (5) Method of denoting the number of components in compound (double, triple, etc.) salts. (6) Nomenclature of (*a*) salts of condensed acids, (*b*) special groups of elements. (7) Method of writing long names. (8) Use of old names. (9) Method of denoting water of crystallisation. T. S. P.

Chemical and Biological Effects of Ultra-violet Light. MAURICE LOMBARD (*Compt. rend.*, 1910, **150**, 227—229. Compare Courmont, Abstr., 1909, ii, 753; Aubel, this vol., ii, 28).—Owing to the contradictory results obtained by previous observers, the author has re-examined the chemical effects of quartz-mercury lamps on water. The sterilising action of the Kromayer lamp has been ascribed to the formation of hydrogen peroxide; it has been found, however, that the production of iodine from potassium iodide is more marked with a feebly alkaline, natural water than when the water is slightly acidified. Distilled water gave comparable results only after addition of a nitrate. The liberation of iodine, therefore, appears to be due to the formation of nitrites, and this has been confirmed by the production of a coloration with sulphanilic acid and α-naphthylamine. Hydrogen peroxide is probably formed first, in accordance with the equation: $2H_2O = H_2O_2 + H_2$, and this is followed by reduction of the nitrate. The sterilising action of the lamps is considered to depend on the direct action of the rays on bacteria. W. O. W.

Utilisation of Electrolytic Chlorine for the Simultaneous Production of Hydrochloric and Sulphuric Acids. ANGELO COPPADORO (*Gazzetta*, 1909, **39**, ii, 616—642).—The author discusses the various processes devised for utilising the chlorine yielded by the electrolytic soda industry, and describes his own investigations on the reaction expressed by the equation:

$$Cl_2 + SO_2 + 2H_2O = 2HCl + H_2SO_4.$$

Study of the equilibrium between the three components, water and sulphuric and hydrochloric acids, in the liquid phase at 17°, 40°, and 70° shows that, with increasing proportions of sulphuric acid, the solubility of the hydrochloric acid undergoes considerable diminution. The amount of such diminution cannot, however, be calculated by means of the formulæ given by Nernst (Abstr., 1890, 3) and Noyes (Abstr., 1891, 142), such formulæ giving accurate results only for dilute solutions. With Bodländer's formula (Abstr., 1891, 794, 795), $W/\sqrt[3]{S} = \text{const.}$, where W and S indicate grams of water and hydrochloric acid respectively, the value of the expression is constant only for solutions containing small proportions of sulphuric acid, and increases with the amount of the latter. If, however, allowance is made for the formation of the hydrate H_2SO_4,H_2O in solutions containing much sulphuric acid, the value of W being diminished by the amount of water in this hydrate, approximately constant results are obtained for the expression $W'/\sqrt[3]{S}$.

The industrial application of this process and its economics are discussed. T. H. P.

Solubility of Gases in Concentrated Sulphuric Acid and in Mixtures of Sulphuric Acid and Water. CHRISTIAN BOHR (*Zeitsch. physikal. Chem.*, 1910, **71**, 47—50).—The solubility of nitrogen, oxygen, and carbon dioxide in 96% sulphuric acid, and of the first two gases in mixtures of sulphuric acid and water in varying proportions, has been measured in the neighbourhood of 21°. The results for the 96% acid, in terms of Bunsen's absorption-coefficient × 100, are as follows: carbon dioxide, 92·6; oxygen, 2·748; nitrogen, 1·292, from which it will be seen that the solubilities are not very different from those in water. The solubilities are, however, much less in mixtures of sulphuric acid and water, and for oxygen and nitrogen reach a minimum in $25N$ solution, at which the solubility is less than one-third of that in water. At the same point, the contraction on mixing sulphuric acid and water attains its maximum value. G. S.

Amides of Sulphuric Acid. FRITZ EPHRAIM and M. GUREWITSCH (*Ber.*, 1910, **43**, 138—148. Compare Abstr., 1909, ii, 994).—The methods for preparing sulphamide are far from satisfactory, and the authors have consequently investigated new methods. Theoretically, dimethyl sulphate and ammonia should give rise to sulphamide and methyl alcohol, but instead of these compounds, methylamine and ammonium methyl sulphate are formed. The difficulties met with in the preparation of methyl amidosulphonate, $NH_2{\cdot}SO_2{\cdot}OMe$, were too great to use that compound as the starting point.

Attempts were then made to prepare the chloroamide of sulphuric acid, $Cl{\cdot}SO_2{\cdot}NH_2$. Amidosulphonic acid, $NH_2{\cdot}SO_3H$, and phosphorus pentachloride, in the proportion of 1 : 5 by weight, readily interacted at 70—90°. After filtering the olive-green liquid so obtained through glass wool, it was distilled on the water-bath under diminished pressure. Phosphoryl chloride and phosphorus trichloride passed over, leaving a viscous, dark brown liquid, which deposited white crystals (m. p. 33—34°) after a long time at 0°. The analytical results were only in approximate agreement with the formula $NH_2{\cdot}SO_2{\cdot}Cl + PCl_3$. The compound is very sensitive to water and water vapour, hydrogen chloride, phosphorous acid, and amidosulphonic acid being formed. Boiling sodium hydroxide does not liberate ammonia, which is only produced on prolonged heating with fuming hydrochloric acid in a sealed tube. All attempts to decompose it into its components were unsuccessful.

When thionyl chloride and amidosulphonic acid are heated together in a sealed tube at 105—110°, ammonium chlorosulphonate, $Cl{\cdot}SO_3{\cdot}NH_4$, is formed, and is purified by washing with carbon disulphide or light petroleum, and, after drying, it forms a white mass with a yellowish tinge (m. p. about 152° in sealed tubes). It fumes in the air, and gradually deliquesces. On treatment with liquid ammonia there is a violent reaction, the product of which dissolves in the excess of ammonia. After evaporation of the solvent, the residue is

dissolved in water, the solution acidified with nitric acid, and silver nitrate added in large excess. After collecting the silver chloride, the filtrate is fractionally precipitated with ammonia, the first and smallest fraction being rejected. From a hot solution the precipitate consists of silver sulphamide, $SO_2(NHAg)_2$, whereas from a cold solution it is silver imidosulphamide, $NAg(SO_2{\cdot}NHAg)_2$, with varying amounts of water of crystallisation. Trisulphimide was not found in the reaction products.

When sulphuryl chloride is added drop by drop to liquid ammonia cooled by an ether-solid carbon dioxide freezing mixture, there is a violent reaction according to the equation: $2SO_2Cl_2 + 7NH_3 = NH(SO_2{\cdot}NH_2)_2 + 4NH_4Cl$. No trisulphimide is formed, and, after evaporating off the excess of ammonia, silver imidosulphamide may be obtained from the residue in a manner similar to that already described. It is always contaminated with silver sulphamide, the sulphamide being formed from the imidosulphamide according to the equation: $NH(SO_2{\cdot}NH_2)_2 + H_2O = NH_2{\cdot}SO_3H + SO_2(NH_2)_2$. In fact, silver imidosulphamide may be readily transformed into silver sulphamide by solution in dilute acid and precipitation from the warm solution by ammonia.

Pure sulphamide is best prepared by dissolving the product of the reaction between sulphuryl chloride and liquid ammonia in a small quantity of water and making the solution just acid. After two to three days the hydrolysis is complete, the mixture is evaporated to dryness in a vacuum, and the residue extracted with ethyl acetate, which dissolves out the sulphamide, amidosulphonic acid and ammonium chloride being insoluble. After evaporating off the ethyl acetate, pure sulphamide, m. p. 93°, is left.

Pure silver imidosulphamide was prepared by extracting the product of the reaction between sulphuryl chloride and liquid ammonia with ethyl acetate in order to remove the sulphamide, and then working up the residue at the ordinary temperature to silver imidosulphamide in the manner already indicated. It contained $4 6H_2O$.

When a solution of amidosulphonic acid is neutralised with ammonia, and the calculated quantity of silver nitrate added to form the silver salt, no precipitate forms until the liquid has been evaporated to a syrupy consistence. It then solidifies suddenly to a radiating crystalline mass, which, after crystallisation from water, gives rhombohedral crystals of silver ammonium amidosulphonate,

$$NH_2{\cdot}SO_3Ag,NH_2{\cdot}SO_3NH_4.$$

T. S. P.

Allotropy of Tellurium. Ernst Cohen and J. F. Kröner (*Chem. Weekblad*, 1910, 7, 57—61).—A summary of the literature on the allotropy of tellurium. A. J. W.

Behaviour of Nitric Oxide at Low Temperatures. Karol Adwentowski (*Bull. Acad. Sci. Cracow*, 1909, 742—767).—The gas investigated by the author was prepared by the action of nitric acid on ferrous sulphate or of sulphuric acid on a solution containing potassium iodide and potassium nitrite, and was purified by condensation and fractional distillation.

The relative density of nitric oxide remains unchanged when the temperature is lowered to about $-150°$. The mean coefficient of expansion at 760 mm. between $-140°$ and $0°$ is 0·0037074. Liquid nitric oxide is colourless in thin layers, and light blue when examined in thick layers. It is, however, probable that the blue colour is due to traces of nitrogen trioxide which cannot be removed by fractionation. The critical temperature is $-92·9°$, the critical pressure 64·6 atmospheres. It boils at $-150·2°$, and solidifies at $-160·6°$. The vapour pressure at this temperature being 168 mm. of mercury.

The vapour-pressure curve of liquid nitric oxide is somewhat anomalous, and this is attributed to polymerisation of the molecules at low temperatures. The fact that the vapour density at atmospheric pressure is quite normal at these temperatures indicates, however, that the dissociation of the polymerised molecules is practically complete at this pressure. The high density of the liquid at its boiling point, D 1·269, is cited as evidence in support of the view that the liquid molecules are associated. H. M. D.

Molecular Weight of Nitrous Acid in Aqueous Solution. ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1704—1708).—That the molecule of nitrous acid in aqueous solution is represented by the formula HNO_2 is partly confirmed by Schümann's measurements of the electrical conductivity and affinity constant of the acid (Abstr., 1900, ii, 264). Simple shaking of solutions of nitrous acid with chloroform results in the expulsion of the anhydride, N_2O_3, the appearance of which is explainable as due either to the occurrence of the anhydride in the solution or to the slight stability of the acid and its consequent decomposition into water and nitrogen trioxide under the influence of the chloroform. Cryoscopic measurements of aqueous solutions of nitrous acid give the molecular weights 46 0, 46·6, and 46·6, which are very nearly identical with the value, 47, required by the formula HNO_2. T. H. P.

Compounds of Sulphur and Phosphorus. V. Tetraphosphorus Trisulphide, P_4S_3. ALFRED STOCK [with MAX RUDOLPH] (*Ber.*, 1910, **43**, 150—157).—The author has shown previously that the only three compounds of phosphorus and sulphur are P_4S_3, P_4S_7, and P_2S_5 (P_4S_{10}) (compare Abstr., 1909, ii, 569). The present communication describes the preparation and properties of the first compound, tetraphosphorus trisulphide.

An excess of red phosphorus is mixed with finely-powdered sulphur, and the mixture heated in a wide tube, sealed at one end, in an atmosphere of carbon dioxide. The temperature is first gradually raised to 100°, and then the reaction started by stronger local heating near the surface of the mixture. When the reaction has spread through the whole mass, the tube is strongly heated until the contents begin to distil, otherwise higher sulphides of phosphorus are formed; the reaction product, which consists of red phosphorus and tetraphosphorus trisulphide, is allowed to cool in the atmosphere of carbon dioxide. The trisulphide may be separated from the red phosphorus by extraction with carbon bisulphide or by distillation in an

atmosphere of carbon dioxide, but in both cases it is somewhat impure.

After purification and recrystallisation from benzene, a pure light-yellow product is obtained, which sinters at 171·5°, m. p. 172·5°.

The b. p. is 407—408°/760 mm., but at the same time there is slight decomposition, as indicated by a variation in the melting point. $D^{17} = 2·03$. The molecular weight, both in carbon disulphide solution and as vapour, corresponds with the formula P_4S_3. At 17°, 1 part by weight of P_4S_3 is dissolved by 1, 40, and 32 parts by weight respectively of carbon disulphide, benzene, and toluene. The concentrated solutions are intensely yellow.

Tetraphosphorus trisulphide is decomposed by both concentrated and dilute potassium hydroxide solution, hydrogen and phosphine (1 : 1 to 2 : 1) being evolved. The evolution of gas lasts for days at the ordinary temperature. If the brownish-red solution is acidified immediately after being prepared, a yellow precipitate, resembling solid phosphorus hydride, $P_{12}H_6$, is obtained, which decomposes and becomes brown after a time. This precipitate is not obtained from solutions which have been preserved for some time. T. S. P.

Compounds of Sulphur and Phosphorus. VI. Tetraphosphorus Heptasulphide, P_4S_7. ALFRED STOCK [with BERLA HERSCOVICI] (*Ber.*, 1910, **43**, 414—417).—An intimate mixture of purified red phosphorus and sulphur, in such proportions that the reaction product would consist of $P_4S_7 + 5\% \; P_4S_3$, is heated in a hard glass tube in the way described in the preparation of tetraphosphorus trisulphide (preceding abstract) until distillation begins. The cooled product is then recrystallised from carbon disulphide, in which the heptasulphide is sparingly soluble (1 part in 3500 parts solvent at 17°, and 1 part in 20,000 parts at 0°), whilst the trisulphide is readily soluble.

Tetraphosphorus heptasulphide crystallises in small, slightly yellow prisms, $D^{17} = 2·19$, sinters at 305—308°, m. p. 310°.

The b. p. is 523°/760 mm., and the vapour density at 700° corresponds with the formula P_4S_7; above 750° the vapour density rapidly diminishes to one-half its normal value. At the ordinary temperature, it is stable, but on melting, and at higher temperatures, it decomposes to some extent. It is more sensitive to moisture than the trisulphide. When exposed to the air for some time, it smells strongly of hydrogen sulphide. T. S. P.

Crystalline Boron. II. HEINRICH BILTZ (*Ber.*, 1910, **43**, 297—306).—So-called crystalline boron has hitherto been obtained in two different crystalline forms, the one being black and having the formula AlB_{12}, whilst the other consisted of colourless to yellow, quadratic crystals, having the composition $C_2Al_3B_{48}$ (Hampe, this Journ., 1877, i, 273). The preparation of the colourless crystals has hitherto been a very troublesome matter, but the author obtains them readily as follows: A mixture of 50 grams of boron trioxide, 75 grams of sulphur, 100 grams of aluminium, and 2 grams of soot is fired by an

appropriate fuse. The fused mass is treated with water and concentrated hydrochloric acid, and the residue finally left under dilute hydrochloric acid for some days. When all action has ceased, it is well washed by decantation with hot water. The resulting preparation consists mostly of the transparent, yellow, quadratic crystals, but it is also mixed with the black crystals. The black crystals have $D_4^{18} = 2\cdot554 \pm 0\cdot005$, and the yellow, $D_4^{18} = 2\cdot590 \pm 0\cdot006$, and are separated by the flotation method in a mixture of methylene iodide and benzene.

The quadratic crystals are not attacked by hot concentrated hydrochloric acid or sulphuric acid, or by a solution of chromium trioxide in concentrated sulphuric acid. They are dissolved by hot concentrated nitric acid, especially when heated in a sealed tube at 150—180°. In transmitted light they are yellow to brownish-yellow in colour, whereas in reflected light they are dark brown to grey. Analysis gave 4·07% C, 13·38% Al, and 82·1% B (= total of 99·6%), which corresponds with the formula $C_2Al_3B_{44}$, which is slightly different from that obtained by Hampe (*loc. cit.*). It is not possible to say whether these crystals are a definite chemical compound or a saturated mixed crystal. T. S. P.

Action of Carbon Tetrachloride Vapour on Anhydrides and Oxides. PIERRE CAMBOULIVES (*Compt. rend.*, 1910, **150**, 175—177). —The author gives in tabular form a list of those oxides which undergo conversion into chlorides or oxychlorides when heated in a stream of carbon tetrachloride vapour; the nature of the products is indicated, as well as the temperature at which the reaction commences. No action occurs with the oxides of boron and silicon. In other cases, chlorination occurs between 215° and 580°. The oxides of niobium and thorium give a mixture of oxychloride and chloride, whilst tungstic oxide gives the oxychloride only. All the other metallic oxides examined yielded the corresponding chloride.

W. O. W.

Action of Carbon Tetrachloride Vapour on Minerals. PIERRE CAMBOULIVES (*Compt. rend.*, 1910, **150**, 221—223. Compare preceding abstract).—The ease with which natural or artificial metallic oxides undergo chlorination when heated in carbon tetrachloride vapour renders possible the application of this substance to the analysis of complex minerals. A separation of free and combined silica in bauxite, for example, can be effected in this way, since aluminium silicate is transformed into the chlorides of aluminium and silicon, whilst uncombined silica is not attacked. In the same manner, molybdenite has been shown to contain free molybdenum oxide. W. O. W.

Conductivity of the Inner Cone of Divided Flames. The Explosibility of Gaseous Mixtures. FRIEDRICH EPSTEIN and P. KRASSA (*Zeitsch. physikal. Chem.*, 1910, **71**, 28—46).—The authors describe the experimental work on which the conclusions of Haber (this vol., ii, 122) as to the connexion between luminosity and electrical conductivity in the Bunsen flame are partly based.

A steady flame was secured by thorough mixing of the coal-gas and

air before reaching the burner. As electrodes for the conductivity measurements, two platinum-iridium wires 0·05 mm. in diameter were stretched horizontally across the flame; they were fixed 1—2 mm. apart, and the position of the cone of the flame with reference to them could be altered by means of a screw arrangement. In order to minimise the effect of the ends of the electrodes, and thus obtain more regular results, 3 cm. in the middle of each wire was covered with magnesium oxide. Measurements of temperature were made simultaneously by means of a thermo-couple.

As the electrodes are gradually lowered in the flame, the electrical conductivity increases regularly, but there is a sudden increase when the electrodes reach the luminous cone. In one experiment with the electrodes 1 mm. apart, the conductivity was three to four times greater at the summit of the luminous zone than at a point 1 mm. above it. As the proportion of oxygen in the mixture is gradually diminished, the change of conductivity on reaching the luminous zone is less abrupt, a result which is due in part to the lowering of temperature. The addition of carbon dioxide to the gas mixture also renders the change of conductivity at the margin of the luminous zone less sharp, but at the same time broadens out the luminous zone, so that in this case, also, there is a close connexion between conductivity and luminosity. Further, in the case of the carbon monoxide flame, which is only slightly luminous, there is no great increase of conductivity on reaching the inner cone.

Contrary to the general opinion as to the action of an inert gas on the luminosity of a flame, it was found that when the supply of gas and air was kept constant, and carbon dioxide was added to a flame, it became more explosive, and it is even possible in this way to bring about the separation of an undivided flame. This conclusion is borne out by the results of Eitner (*Habilitationsschrift*, München, 1902), which are discussed at length. In this connexion, it is shown that Le Chatelier's rule, according to which the lower limit of explosibility of a gaseous mixture is an additive function of its composition, is approximately valid, but this rule does not hold for the higher limit of explosibility. G. S.

Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation. SEBASTIAN TANATAR, *Ber.*, 1910, **43**, 127—128).—Riesenfeld and Reinhold (this vol., ii, 33) class the potassium percarbonate of Constam and Hansen as a real percarbonate, because it liberates iodine immediately from neutral potassium iodide, whereas Tanatar's sodium percarbonate does not react in this way, and is therefore considered to be a carbonate with hydrogen peroxide of crystallisation.

The author points out that these reactions prove nothing, and could be foreseen. Potassium percarbonate ($K_2C_2O_6$) forms potassium hydrogen carbonate in aqueous solution, and this would have no action on iodine, whereas not hydrogen carbonate, but carbonate is contained in aqueous solutions of Tanatar's sodium percarbonate. The carbonate would prevent the liberation of iodine owing to the formation of hypoiodite; the latter compound would then react with hydrogen

peroxide with evolution of oxygen, as observed by Riesenfeld and Reinhold.

The author states that he does not bind himself to any particular conception of the constitution of his percarbonates. T. S. P.

So-called Amorphous Silicon. ERNST WILKE-DÖRFURT (*Festschrift Otto Wallach*, 1909, 671—684).—The form of silicon which is obtained in the reduction of silicon fluoride by sodium at a dull red heat reacts readily with sulphuric acid and with hot water. In the former case, sulphur is formed as one of the reduction products. The great readiness with which the silicon reacts on these substances explains the poor yields which have been obtained by previous workers who have prepared amorphous silicon by this process. It also prevents this process from being economically used for the preparation of large quantities of the reactive amorphous form.

A similar amorphous product is obtained with a comparatively high yield when sodium silicofluoride is melted together with sodium and aluminium, and the metallic regulus obtained is treated with acids. This first product, of a grey colour, is not very reactive, and on that account it can be separated more or less completely from admixed silica. When heated with hydrofluoric acid, the greyish-coloured variety of silicon is, however, converted into a brown variety, which is very much more reactive. The product thus obtained is violently attacked by concentrated nitric acid, with the formation of a white substance which appears to be a nitride, since it evolves ammonia when acted on by sodium hydroxide. When heated, the brown, amorphous silicon is transformed into a much less active form.

Many apparently conflicting statements in the literature can be explained on the basis of the author's observations. H. M. D.

Alloys of the Chlorides of the Alkali Metals. S. F. SCHEMTSCHUSCHNY and F. RAMBACH (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1785—1814. Compare Kurnakoff and Schemtschuschny, Abstr., 1906, ii, 443).—The authors have traced the melting-point and solidification curves of binary mixtures of the chlorides of the alkali metals.

For lithium and potassium chlorides, the m. p. diagram consists of two branches meeting at the eutectic point 352°, which corresponds with 40·5 mol. % KCl and 59·5 mol. % LiCl. Solid solutions are not formed, the two components separating from the molten mixtures in the pure state. The molecular depression of the m. p. of lithium chloride (100 mols.) by potassium chloride is 4·5—4·3°, whilst with potassium chloride as solvent, the molecular depression is 4·9—4·8°. The eutectic alloy, m. p. 352°, furnishes a good protecting layer for metals which oxidise on heating to 400—500°. The m. p. of lithium chloride is 614° (Carnelley, this Journ., 1876, i, 489, found 602 ± 5°, and Guntz, *Zeitsch. angew. Chem.*, 1898, **11**, 158—159, 600°).

With lithium and rubidium chlorides, the curve is composed of two branches, which meet at the eutectic point 312°, corresponding with 44·75 mol. % RbCl and 55·25 mol. % LiCl; no solid solutions are formed. The molecular depression for lithium chloride is 4·3—4·1°,

and for rubidium chloride, 4·6—4·3°. Rubidium chloride has m. p. 726° (Carnelley, Trans., 1878, **33**, 273, found 710°).

For lithium and sodium chlorides the cooling curves exhibit no eutectic halt, solidification proceeding over a certain interval of temperature, and solid solutions of various concentrations being formed. The m. p. diagram is a continuous curve of Roozeboom's type III, exhibiting a minimum at 552°, corresponding with 27 mol. % NaCl. The molecular depression of the m. p. of sodium chloride is 3·8—3·7°, and of the lithium salt, 2·5°.

With rubidium and potassium chlorides the m. p. curve is continuous, and proceeds at first almost horizontally and then gradually rises to the m. p. of potassium chloride. Solid solutions are formed in all proportions of the components, the m. p. curve being of Roozeboom's type I. These observations are confirmed by the structures of the alloys. The molecular depression of rubidium chloride is in this case negative and equal to 0·15—0·11°, whilst for the potassium salt it amounts to 1·4—1·3°.

The m. p. diagram of rubidium and sodium chlorides consists of two branches meeting at the eutectic point 541°, which corresponds with 54·96 mol. % RbCl. The molecular depression is 4·4—4·0° for rubidium chloride, and 4·3—4·1° for sodium chloride.

Cæsium chloride has m. p. 646° (Carnelley and Williams, Trans., 1880, **37**, 125, gave 631°). The cooling curves for mixtures of rubidium and cæsium chlorides exhibit two halts, the second, at 451°, being conditioned by the existence of a polymorphous modification of cæsium chloride. The ratio of the heat of transformation into this second modification to the latent heat of fusion of cæsium chloride is found to be 0·35. The m. p. diagram is a continuous curve of Roozeboom's type III, and exhibits a minimum at 440°, corresponding with 11·5 mol. % of rubidium chloride. The molecular depression for cæsium chloride is 1·6—1·5°, and for rubidium chloride, 1·6—1·5°.

With cæsium and potassium chlorides, the m. p. diagram is a continuous curve (Roozeboom's type III) with a minimum at 616°, corresponding with 34 mols. % KCl. None of the cooling curves show a eutectic halt, solid solutions of various concentrations being formed. The presence of potassium chloride lowers the temperature of polymorphous transformation of cæsium chloride; with 11·5 mol. % of KCl, the change becomes very indistinct, and with higher proportions disappears completely. The molecular depression is 1·1° for cæsium chloride and 2·8—2·9° for potassium chloride.

For sodium and cæsium chlorides the m. p. diagram is formed of two branches meeting at 493°, which corresponds with 34·5 mol. % NaCl; no solid solutions are formed. Similar results are obtained with the system CsCl + LiCl.

These chlorides may be divided into two groups: (1) those of potassium, rubidium, and cæsium, which mix in all proportions, and (2) those of lithium and sodium, which at high temperatures form uninterrupted series of solid solutions, these decomposing at lower temperatures.

By means of van't Hoff's formula, the latent heats of fusion are

found to be: for NaCl, 97; LiCl, 86; KCl, 63; RbCl, 38, and CsCl, 24 Cals., these values diminishing with increase of the molecular weight.

The heats of formation of a number of the solid solutions formed by the above salts have been measured, and it is found that, in all cases, considerable absorption of heat occurs, the solid solutions being consequently unstable and undergoing gradual decomposition.

T. H. P.

Some Thiophosphates. FRITZ EPHRAIM and ETTA MAJLER (*Ber.*, 1910, **43**, 285—288).—When solid sodium tetrathiophosphate, Na_3PS_4 (compare Abstr., 1905, ii, 318), is treated with the solutions of sulphides of other metals, reaction takes place either according to the equation $2Na_3PS_4 + 3M_2S + 2H_2O = 2M_3PS_3O + 3Na_2S + 2H_2S$, or according to the equation: $2Na_3PS_4 + 3M_2S + 4H_2O = 2M_3PS_2O_2 + 3Na_2S + 4H_2S$. In no case is the tetrathiophosphate of the second metal formed, owing to hydrolysis by the water.

Barium oxytrithiophosphate, $Ba_3(PS_3O)_2,20H_2O$, was obtained from sodium tetrathiophosphate and a solution of barium sulphide. It is stable when dry, but is decomposed by water or dilute acids with evolution of hydrogen sulphide. Concentrated nitric acid dissolves it, the sulphur being completely oxidised to sulphuric acid. When barium hydrosulphide is used instead of the sulphide, *barium dioxydithiophosphate*, $Ba_3(PS_2O_2)_2,18H_2O$, is obtained (compare Stock, Abstr., 1906, ii, 535). Attempts to prepare strontium and calcium thiophosphates were unsuccessful.

Magnesium oxytrithiophosphate, $Mg_3(PS_3O)_2,20H_2O$, was obtained from magnesium hydrosulphide. It was precipitated from solution by alcohol in the form of white needles. It is decomposed by water or dilute acids.

T. S. P.

Selenophosphates. FRITZ EPHRAIM and ETTA MAJLER (*Ber.*, 1910, **43**, 277—285).—Selenophosphates of the alkali and alkaline-earth metals and of magnesium can be prepared by the action of phosphorus pentaselenide on aqueous solutions of the selenides of the respective metals, the reaction proceeding according to the equation: $3M_2Se + P_2Se_5 = 2M_3PSe_4$. In no case, however, could a solid tetraselenophosphate be obtained, water decomposing it thus: $M_3PSe_4 + H_2O = M_3PSe_3O + H_2Se$. In some cases the decomposition may go further still, with the formation of the compound $M_3PSe_2O_2$, or even M_3PSeO_3. In many cases intermediate compounds, for example, $K_3PSe_{2\cdot5}O_{1\cdot5}$, are formed, which the authors consider may be isomorphous mixtures of the different oxyselenophosphates. If the compounds crystallise from a mother liquor rich in hydrogen selenide, they are also rich in selenium, but if precipitated by alcohol they are poorer in selenium.

The oxyselenophosphates may also be prepared from the hydroxide of the metal and phosphorus pentaselenide. Even in the presence of excess of alkali, the normal salts sometimes hydrolyse with the formation of the monohydrogen salts, the process being conditioned by the relative solubilities of the two salts in the mother liquor.

On solution in water, especially in hot water, all the compounds decompose according to the equation: $M_3PSe_4 + 4H_2O = M_3PO_4 +$

$4H_2Se$. The mother liquors oxidise quickly on exposure to the air, becoming red and depositing selenium. The solid salts are fairly stable in dry air.

Normal salts were only obtained with the alkali metals; the alkaline-earth metals give monohydrogen salts.

An ammonium tellurophosphate could not be obtained.

Sodium trioxyselenophosphate, $Na_3PSeO_3,20H_2O$, was prepared by digesting a strong solution of sodium hydroxide with phosphorus pentaselenide. The same substance was obtained when sodium hydroselenide was used in the place of sodium hydroxide. It crystallises in needles.

Ammonium oxytriselenophosphate was obtained from phosphorus pentaselenide and a saturated solution of hydrogen selenide in strong ammonia. From the warm mother liquor, leaflets crystallised having the composition $(NH_4)_3PSe_3O,10H_2O$, and later the cold mother liquor deposited octahedra and four-sided leaflets of the composition $(NH_4)_5H(PSe_3O)_2,18H_2O$.

Potassium oxyselenophosphate, $K_3PSe_{2\cdot5}O_{1\cdot5},H_2O$, was obtained in the form of greenish-yellow octahedra by using potassium hydroselenide. It reacts violently with nitric acid.

Barium dioxydiselenophosphate, $BaHPSe_2O_2,14H_2O$, is formed when phosphorus pentaselenide is treated either with a solution of barium hydroxide, or with a saturated solution of hydrogen selenide in barium hydroxide. It forms a white, micro-crystalline powder.

When 2 grams of strontium hydroxide, dissolved in a little water, were treated with 3 grams of phosphorus pentaselenide and the filtrate from the deposited selenium treated with alcohol, a light yellow precipitate of a *strontium oxyselenophosphate*, having the composition $SrHPSe_{2/3}O_{10/3},7H_2O$, was obtained. When a larger excess of the pentaselenide was used, the crystals were colourless, and had the composition $SrHPSe_{4/3}O_{8/3},8H_2O$, which may possibly be

$$2SrHPSeO_3,SrHPSe_2O_2,24H_2O.$$

With calcium hydroxide a *calcium oxyselenophosphate* was formed. With the smaller proportion of phosphorus pentaselenide, the yellow crystals obtained had the composition $CaHPSe_{1/3}O_{11/3},5H_2O$, whilst with the larger proportion their composition was $CaHPSeO_3,8H_2O$.

A *magnesium dioxydiselenophosphate* was also obtained, but not in a pure condition. T. S. P.

Lithium Phosphomolybdates. FRITZ EPHRAIM and MAX BRAND (*Zeitsch. anorg. Chem.*, 1910, **65**, 233—236).—Five lithium phosphomolybdates, two of which are of rather complicated composition, have been prepared.

The *salt*, $3Li_2O,P_2O_5,5MoO_3$, with both $16H_2O$ and $17H_2O$, is obtained from the mother liquor of its additive compound, described below, in white prisms. The *salt*, $5Li_2O,2P_2O_5,8MoO_3,28H_2O$, is obtained when lithium carbonate, phosphoric acid, and molybdenum trioxide are mixed in the proportions of the first salt, and the solution is evaporated. It forms long, slender needles, readily soluble in water. The *salt*, $3Li_2O,P_2O_5,12MoO_3,18H_2O$, is obtained on adding dilute nitric acid to the first salt in concentrated solution, and forms a yellow,

micro-crystalline precipitate. When the mother liquor is evaporated, orange crystals of the *salt*, $3Li_2O,P_2O_5,18MoO_3,27H_2O$, are obtained.

The *double* salt, $3Li_2O,P_2O_5,5MoO_3 + 6Li_3PO_4,18H_2O$, is obtained when 52 grams of lithium molybdate are dissolved, and 29 grams of molybdenum trioxide and 15 grams of phosphoric oxide added. It crystallises in short rods, and has an alkaline reaction, whilst the other lithium phosphomolybdates are acid. Water decomposes it, leaving a residue of lithium phosphate. C. H. D.

Rubidium and Cæsium Phospho- and Arseni-molybdates. FRITZ EPHRAIM and HEINRICH HERSCHFINKEL (*Zeitsch. anorg. Chem.*, 1910, **65**, 237—247).—The *salt*, $7Rb_2O,P_2O_5,22MoO_3,12H_2O$, is obtained by mixing the components in the molecular proportions 3 : 1 : 2, when a yellow salt, usually slightly green owing to partial reduction, is precipitated. By the addition of nitric acid, D 1·2, to a solution of rubidium phosphomolybdate, a yellow precipitate of the salt,

$$3Rb_2O,P_2O_5,20MoO_3,12H_2O,$$

is obtained. If this salt is suspended in water, and rubidium carbonate is added until the yellow colour of the solid disappears, a white *salt*, $6Rb_2O,P_2O_5,18MoO_3,10H_2O$, is obtained. If 0·5 mol. phosphoric acid is added to 1 mol. rubidium carbonate, and then boiled with 1 mol. molybdenum trioxide, a solution is formed which deposits very large crystals of the *salt*, $5Rb_2O,2P_2O_5,9MoO_3,13H_2O$. The last portions of the mother liquor deposit crystals of $7Rb_2O,3P_2O_5,10MoO_3,15H_2O$.

A yellow *caesium* salt has the composition

$$2Cs_2O,P_2O_5,14MoO_3,3H_2O.$$

A white *salt*, $3Cs_2O,P_2O_5,6MoO_3,8H_2O$, is obtained similarly to the white rubidium salt.

A simple *rubidium arsenomolybdate*, $Rb_2O,As_2O_5,6MoO_3$, is obtained as a white, micro-crystalline precipitate by adding rubidium nitrate to a concentrated solution of arsenomolybdic acid (Pufahl, Abstr., 1884, 715). A *salt*, $4Rb_2O,As_2O_5,18MoO_3,40H_2O$, is obtained as a yellow precipitate by mixing molecular proportions of rubidium hydroxide and molybdenum trioxide, and then adding nitric acid and arsenic acid. If an excess of arsenic acid is used, colourless crystals of the *salt*, $3Rb_2O,3As_2O_5,5MoO_3,9H_2O$, are obtained, readily soluble in water. It contains more arsenic than any previously known arsenomolybdate.

A yellow *caesium arsenomolybdate*, $4Cs_2O,As_2O_5,26MoO_3,15H_2O$, is obtained in similar manner. It was not found possible to prepare a white cæsium salt, the product isolated being *caesium arsenate*, $Cs_2O,2As_2O_5,5H_2O$, which forms well-developed crystals. C. H. D.

Dimorphism of Ammonium Haloids. ROBERT C. WALLACE (*Centr. Min.*, 1910, 33—36).—When ammonium chloride is sublimed there is a marked change in the heat effect at 159° ; under the microscope the crystals exhibit a change at this temperature, although they still remain optically isotropic ; and on cooling in a dilatometer filled with oil, the crystals show an appreciable contraction in volume at this point. Ammonium bromide exhibits the same reversible phenomena at 109°, but ammonium iodide shows no change.

The molecular volumes of ammonium chloride and ammonium

bromide in their modifications stable at the ordinary temperature indicate that these (more highly polymerised) salts are not isomorphous with the potassium haloids and ammonium iodide; but it is probable that the modifications stable at the higher temperatures do belong to this isomorphous series. L. J. S.

Properties of Precipitated Silver. TARAK NATH DAS (*Chem. News*, 1910, **101**, 51).—When the solution of hypophosphite obtained in the preparation of phosphine from phosphorus and sodium hydroxide is acidified and treated with silver nitrate, a yellow precipitate of silver separates after a time, and gradually changes in colour, becoming successively brown, red, grey, and finally black. The precipitate dissolves very readily in solutions of potassium cyanide and potassium chlorate, less readily in sodium thiosulphate, and is nearly insoluble in ammonia and sodium hydroxide. H. M. D.

Atomic Weight of Strontium. Sir EDWARD THORPE and ARTHUR G. FRANCIS (*Proc. Roy. Soc.*, 1910, *A*, **83**, 277—289).—The atomic weight of strontium has been determined by measurement of the ratios (1) $SrBr_2 : 2Ag$ (6 determinations), (2) $SrBr_2 : 2AgBr$ (5 determinations), (3) $SrCl_2 : 2Ag$ (6 determinations), (4) $SrCl_2 : 2AgCl$ (5 determinations). The strontium salts were purified by very extensive processes of fractional crystallisation, and all reagents used in connexion with the measurements were freed from possible impurities by suitable methods. From the four ratios, the atomic weight of the metal is found to be $87{\cdot}646 \pm 0{\cdot}0016$.

In order to obtain an independent check on these determinations, two further series were made, depending on the ratio of $SrSO_4$ to $SrCl_2$ and $SrBr_2$ (4 and 3 determinations) respectively. In consequence of the more complicated character of the manipulative processes involved in these estimations, the accuracy obtainable by this method is not so high as in the methods of the first four series. The mean value obtained for the atomic weight is $87{\cdot}645 \pm 0{\cdot}0107$. As a final result, the authors adopt the number 87·65, which is only 0·03 in excess of that obtained by Richards. H. M. D.

Action of some Salts of Ammonium on the Alkaline Earth Carbonates. ETTORE SELVATICI (*Bull. Assoc. Chim. Sucr. Dist.*, 1910, **27**, 669—670).—It is proposed to prepare barium chloride and nitrate, and the corresponding strontium compounds, by heating the carbonates with equal mol. weights of ammonium chloride and nitrate respectively. The barium nitrate may be used for preparing the oxide by heating to redness in a current of oxygen, and the peroxide by merely heating to redness. N. H. J. M.

Electrolysis of Cupric Solutions. OCTAVE DONY-HÈNAULT (*Bull. Soc. chim. Belg.*, 1910, **24**, 56—83).—A reply to Foerster (Abstr., 1909, ii, 314) on behalf of Meyer (Abstr., 1908, ii, 803; 1909, ii, 314). As the result of new experiments, the author concludes that the explanation given by Meyer holds for temperatures below 50°, whilst that due to Foerster, Abel, and others is true for

temperatures near the boiling point. Luther's method of estimating cuprous salts by means of permanganate (Abstr., 1901, ii, 301) gives results concordant with those obtained by weighing the copper which separates when a solution of copper sulphate in dilute sulphuric acid, which has been heated at 200° in presence of copper, is cooled. For neutral solutions, the results obtained by the two methods do not agree. Luther's value for the equilibrium constant Cu/Cu_2 is confirmed. T. A. H.

Coloration of Salts. ANDRÉ RASSENFOSSE (*Bull. Acad. roy. Belg.*, 1909, 1289—1321).—The various theories which have been advanced to account for the colour changes of solutions of cupric and cobaltous salts do not give a full explanation of the subject (compare Donnan and Bassett, Trans., 1902, **81**, 939, and Werner, Abstr., 1909, ii, 49).

In the case of copper sulphate, the colour of a solution is shown to depend (*a*) on the dissociation of the salt, and (*b*) on its hydration. Evidence is brought forward to show that in the case of cupric chloride solutions, colour changes induced by the addition of hydrochloric acid by heating, by the action of alcohol, and in other ways are probably due to the formation of compounds of cupric chloride either with the reagent used or with a product of its own decomposition. In this connexion, reference is made to the additive products of hydrochloric acid with cupric, cobaltous, mercuric, and other chlorides isolated by Engel (Abstr., 1888, 558, 918, 1042, 1248; 1890, 109, and 1892, 569).

The addition of hydrochloric acid to a cold saturated solution of cupric chloride causes the precipitation of either the mono- or di-hydrate of cupric chloride, so that the colour change caused by the addition of the acid cannot be due to dehydration of the salt. Further, addition of a dehydrating agent, such as phosphoric oxide, induces no colour change in cupric chloride solution. Zinc chloride added to a green solution of cupric chloride containing hydrochloric acid restores the blue colour, probably because the zinc chloride destroys the cupric chloride hydrochloride existing in the green solution. Sodium, potassium, or barium chloride does not react in the same way as zinc chloride, but calcium or magnesium chloride changes the blue colour of an aqueous solution of cupric chloride to green, probably by the formation of a molecular compound of the two salts. A mixture of saturated solutions of cupric and calcium chlorides deposits after a time a mass of greenish-brown, deliquescent needles of the *double* salt, $2CuCl_2,CaCl_2,6H_2O$. When a solution of cupric chloride in water is boiled, the colour changes to green, the water vapour evolved contains hydrogen chloride, and the boiled solution on cooling shows less absorption for light and an increased electrolytic resistance. Such a solution contains cupric oxide. The blue colour is restored to the hot solution if zinc or mercuric chloride is added. A solution of anhydrous cupric chloride in ethyl alcohol deposits on evaporation under reduced pressure greenish-yellow crystals of an *additive product*, $CuCl_2,2C_2H_5{\cdot}OH$, and a similar *product* is formed with *iso*butyl alcohol. It is probably to the existence of the former substance that

the green colour of an aqueous solution of cupric chloride to which alcohol has been added is due. Cupric chloride is decomposed by paper, and to this cause is due the brown stain produced on drying paper which has been soaked in cupric chloride solution. Similar evidence in favour of the view that colour changes in cupric chloride solution are due to the formation or decomposition of compounds of the type indicated, is afforded by comparison of the absorption spectra and electrolytic resistances of such solutions. T. A. H.

Reactions in Non-Aqueous Solutions. V. In Ethyl Acetate. ALEXANDER NAUMANN [with MAX HAMERS and EMIL HENNINGER] (*Ber.*, 1910, **43**, 313—321. Compare Abstr., 1909, ii, 1018).—The anhydrous ethyl acetate used distilled at 74·5°/750 mm., and had $D_4^{18}=0{\cdot}8995$. For the experiments, half-saturated solutions were used. A list is given of salts which are soluble or insoluble in ethyl acetate.

When hydrogen sulphide is passed into strongly ammoniacal ethyl acetate, a precipitate of ammonium hydrosulphide, in the form of white leaflets, is obtained. The colourless liquid gradually becomes yellow, owing to the formation of polysulphide. The same compound is formed when ammonia is passed into a solution of hydrogen sulphide, but it then crystallises in needles. With hydrogen chloride the ammoniacal solution of ethyl acetate gives a precipitate of ammonium chloride.

At 18° a saturated solution of mercuric chloride in ethyl acetate contains one part of solute to 2·05 parts of solvent. With hydrogen sulphide, a white compound, $HgCl_2,2HgS$, is produced, and with ammonia the compound $HgCl_2,2NH_3$. Hydrogen sulphide and ammonia together give a greyish-black precipitate of mercuric sulphide. Molecular-weight determinations by the boiling-point method gave 254·9—269·2 as the molecular weight of mercuric chloride when dissolved in ethyl acetate.

Mercuric bromide dissolves in ethyl acetate to the extent of one part in 7·66 at 18°. Hydrogen sulphide gives a yellow precipitate of the composition $HgBr_2,2HgS$, and ammonia a white precipitate with the composition $HgBr_2,2NH_3$. Ammonia and hydrogen sulphide together give a precipitate of mercuric sulphide. The molecular weight of the dissolved mercuric bromide was found to be 330·0—351·4 by the boiling-point method.

Mercuric iodide dissolves in ethyl acetate to the extent of 1 part in 68·03 at 18°, and has the molecular weight 413·7—442·3. Hydrogen sulphide gives a yellowish-red precipitate, which probably has the composition $HgI_2,2HgS$. No precipitate is produced with ammonia. Ammonia and hydrogen sulphide together give a precipitate of mercuric sulphide; at first the precipitate is black, but on continued passage of ammonia, it turns red.

Saturated solutions of potassium mercuri-iodide in ethyl acetate do not give a precipitate with either ammonia or hydrogen sulphide. With both these gases together a black precipitate is produced, which contains mercury and sulphur.

At 18° the saturated solution of cadmium iodide in ethyl acetate has $D_4^{18}=0{\cdot}9145$, and contains 1 part of solute in 54·3 parts of solvent.

With hydrogen sulphide it gives a yellow precipitate of the composition $CdI_2,2CdS$. With ammonia the compound $CdI_2,2NH_3$ is precipitated. Ammonia and hydrogen sulphide together produce a precipitate of cadmium sulphide mixed with ammonium hydrosulphide. Hydrogen chloride produced no precipitate, but a slight liberation of iodine. Chlorine gave a white, flocculent precipitate of cadmium chloride, as also did mercuric chloride and bismuth trichloride. Bromine gave a dark-coloured liquid, but there was no evidence of reaction.

At 18° a saturated solution of stannous chloride in ethyl acetate contains 1 part of stannous chloride to 22·40 parts of ethyl acetate, and has $D_4^{18} = 0·9215$. With hydrogen sulphide a brown precipitate of stannous sulphide is produced, and with ammonia the compound $SnCl_2,2NH_3$. Ammonia and hydrogen sulphide together give a precipitate of stannous sulphide mixed with ammonium hydrosulphide. Hydrogen chloride produces no precipitate. Chlorine and bromine both give stannic salts. Mercuric chloride gives a white precipitate of mercurous chloride, even in the presence of excess of stannous chloride.

At 18° a saturated solution of antimony trichloride in ethyl acetate has $D_4^{18} = 1·7968$, and contains 1 part of solute to 16·97 parts of solvent. No precipitate is produced with hydrogen sulphide, but with ammonia the compound $SbCl_3,3NH_3$ is produced. Ammonia and hydrogen sulphide together give a precipitate of antimony trisulphide mixed with ammonium hydrosulphide. There is no reaction with either hydrogen chloride, chlorine, bromine, iodine, mercuric chloride, or bismuth trichloride.

At 18°, 1 part of bismuth trichloride dissolves in 60·36 parts of ethyl acetate, and the solution has $D_4^{18} = 0·9106$. When kept, the solutions become cloudy, owing to the formation of bismuth oxychloride. Hydrogen sulphide gives a precipitate of bismuth sulphide, and ammonia a precipitate of the composition $BiCl_3,2NH_3$. Ammonia and hydrogen sulphide together give bismuth sulphide. Neither hydrogen chloride, chlorine, bromine, iodine, mercuric chloride, nor antimony trichloride have any action. T. S. P.

Action of Heat on Aluminium in a Vacuum. ÉMILE KOHN-ABREST (*Compt. rend.*, 1910, **150**, 169—173).—When aluminium is heated in a porcelain boat at 1100° in a vacuum, the metal is rapidly volatilised at first, but, after some hours, the loss in weight from this cause becomes negligible. After prolonged heating, the residue is found to be coated with a yellow film, consisting of an alloy of aluminium and silicon. The same results are obtained when boats of pure graphite are employed, but only when these are contained in a porcelain tube. The conclusion drawn is that aluminium vapour attacks the porcelain, liberating silicon, which is absorbed by the molten aluminium. The porcelain tubes employed are found to be coated internally with a black, crystalline deposit, from which the compound Al_2Si has been isolated. W. O. W.

Synthetical Production of Sapphires by Fusion. AUGUSTE VERNEUIL (*Compt. rend.*, 1910, **150**, 185—187).—Hitherto, artificial

sapphires have been obtained which owed their colour either to chromium oxide or the iron oxide in a lower state of oxidation than ferric. Those coloured by chromium oxide were obtained by Sainte-Claire Deville and Caron in 1858—1865, but no one has been able to repeat their experiments. The sapphires coloured by iron oxide are of inferior quality.

The author finds that when alumina containing 1·5% of magnetic oxide of iron and 0·5% of titanic acid is fused in the oxyhydrogen flame, which has reducing properties, sapphires are produced which are identical in properties with the natural stones; the colour in this case is due to the presence of the oxides of iron and titanium.

T. S. P.

Do Clays and Cements Adsorb CO_3'' Ions? JOH. D'ANS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 38—40. Compare Rohland, Abstr., 1909, ii, 662).—In reference to the statement of Rohland that carbonates are adsorbed from solutions by cements, experiments were made in which weighed quantities of powdered cements and clays were agitated for several hours with a measured volume of a sodium carbonate solution. After filtration, the hydroxide and carbonate in the solution were determined.

The experimental data show that the dissolved carbonate is partly converted into hydroxide by the free calcium oxide of the cements. In a similar manner, ammonia is set free when the cements are agitated with a solution of ammonium chloride. On the other hand, the clays examined were found to have feebly acid properties, and, as a consequence, small quantities of sodium hydrogen carbonate were found in the solutions after agitation. The author's observations are considered to be incompatible with Rohland's view of carbonate adsorption.

H. M. D.

Formation and Properties of Colloidal Manganese Dioxide. EUGEN DEISS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 69—77).—Stable colloidal solutions of manganese dioxide can be readily obtained by the reduction of permanganate solutions by means of dilute sodium arsenite. They can also be prepared by the oxidation of manganous salts if protective colloids are present in the solution. Various organic colloids can be used for the purpose, and it is also shown that colloidal ferric and aluminium hydroxides act as protective colloids if the amount of manganese in solution is relatively small. If larger quantities of manganese are present, ferric hydroxide behaves quite differently in that it favours the precipitation of the dioxide.

It is probable that the precipitation of manganese dioxide is always preceded by the temporary formation of a colloidal solution of the substance, coagulation resulting as a consequence of the presence of electrolytes. The formation of the iridescent flakes of manganese dioxide, which can be frequently observed in the oxidation or reduction of manganese compounds, is also attributable to the transient formation of a colloidal solution.

The so-called manganites must, in many cases, be regarded as adsorption compounds of manganese dioxide and bases. H. M. D.

The Thermal Formation of Manganates. I. Otto Sackur (*Ber.*, 1910, **43**, 381—388).—A mixture of manganese dioxide with an excess of potassium carbonate was fused in a platinum crucible and maintained at a temperature slightly higher than the melting point of potassium carbonate. At the same time, air or oxygen, or carbon dioxide, or a mixture of these gases, was passed through the fusion by means of a platinum tube. From time to time portions of the fused mass were withdrawn by means of a tube of hard glass, and, after cooling, the percentages of available oxygen and of manganese were determined. The portions withdrawn were taken after the passage of gas had been stopped, and the manganese dioxide still unacted on had been allowed to sink to the bottom of the crucible. In one case the oxide, Mn_3O_4, was used in place of the dioxide. The results show that the absorption of oxygen by the fusion ceases as soon as the atomic proportion of available oxygen to manganese becomes 1·6. This value is independent of the concentration of the manganese in the fusion, and of the partial pressure of the oxygen in the gas above the fusion, so that there does not exist an equilibrium between the different oxidation stages of manganese in the fusion and the oxygen in the gaseous phase, but a definite compound is formed which contains manganese and oxygen in the proportion of 1 : 2·6, and would therefore have the formula

$$Mn_5O_{13} = 2MnO_2,3MnO_3.$$

The fusion is dark green in colour. With a little water or with an alkaline solution, it gives a dark green solution (manganate) and a dark brown precipitate (MnO_2). With much water or dilute acids, a violet solution (permanganate) and manganese dioxide result.

A similar result was obtained when the potassium carbonate was replaced by potassium hydroxide, but with sodium carbonate the atomic proportion of available oxygen to manganese was 1·5 instead of 1·6. A mixture of potassium and sodium carbonates in equal proportions gave the same proportions as with sodium carbonate alone. The fusions containing sodium salts were grass-green in colour, as opposed to the dark green of the potassium compound. Calcium oxide gave similar results to sodium carbonate.

When oxygen is absorbed by the fusion, carbon dioxide is simultaneously evolved, as shown by the equation: $5MnO_2 + \frac{3}{2}O_2 + xK_2CO_3 = Mn_5O_{13},xK_2O + xCO_2$. By estimating the carbon dioxide evolved, it was found that the potassium compound formed in the fusion had the composition $Mn_5O_{13},5K_2O$, whereas the sodium compound was $Mn_2O_5,2Na_2O$. The results obtained also showed that unless the oxygen was passed for a considerable time after the evolution of carbon dioxide had ceased, the compound formed in the fusion was $Mn_5O_{12},5M_2O$, where M is either K or Na.

All the above results are only valid when an excess of alkali carbonate, sufficient to hold the manganese compound formed in solution and so permit of full oxidation, is used.

The complex compounds formed may be considered to be manganic manganates. T. S. P.

The Thermal Formation of Manganates. II. Molecular-Weight Determinations in Fused Alkali Carbonates. OTTO SACKUR (*Ber.*, 1910, **43**, 448—453).—The influence of dissolved salts on the melting points of potassium and sodium carbonates was determined by the method of cooling curves, using a platinum-platinum-rhodium thermocouple. The solutes used with potassium carbonate were potassium chloride, sodium chloride, and sodium carbonate, and with sodium carbonate, potassium chloride, sodium chloride, and potassium carbonate. In each case, with concentrations of the solute up to 1·2 gram-molecules per kilogram of the fusion, the lowering of the freezing point was proportional to the concentration of the solute. The molecular lowering for a binary salt which contains no ion in common with the solvent is approximately twice that for a salt containing a common ion. Ternary salts containing an anion common to the solvent have melting-point constants which are intermediate between those of the two classes of binary salts. These results are in accordance with the views of Goodwin and Kalmus (*Physical Review*, 1909, **28**, 1).

The molecular lowering of the freezing point is 41° in potassium carbonate as solvent, and 31° in sodium carbonate. Sodium chloride dissolved in potassium carbonate is dissociated to the extent of 73%, and potassium chloride in sodium carbonate to 77%. The latent heats of fusion of potassium and sodium carbonates are calculated to be 66 and 82 cals. per gram respectively.

The molecular weights of the complex alkali manganic manganates dissolved in the alkali carbonates (see preceding abstract) were then determined. Pure manganese dioxide was melted with excess of the alkali carbonate and a current of gas consisting of 4/5 oxygen : 1/5 carbon dioxide passed through the fusion for some hours, after which time a portion was removed for analysis, and the melting point of the remainder determined. It was found, when oxidation was complete, that the ratio lowering of the melting point : concentration of the manganese in gram-atoms per 1000 grams of the fusion, was constant and equal to 43 in potassium carbonate and 35 in sodium carbonate. These results show that the solute in each case contains only 1 atom of manganese to the molecule, so that their formulæ must be written $K_2MnO_{3 \cdot 6}$ and $Na_2MnO_{3 \cdot 5}$ respectively, that is, with a fractional number of atoms to the molecule. The full theoretical bearing of this result can only be properly discussed after further experimental results have been obtained. T. S. P.

Cementation of Iron by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1910, **150**, 173—175).—The experiments which have hitherto been made on the cementation of iron by solid carbon have been inconclusive, either because carbonising gases were not eliminated with certainty, or else because it was not proved that the iron and the carbon had been in intimate contact.

The authors proceed as follows : soft Martin steel, containing only traces of elements other than carbon and manganese, and carbon (pure sugar carbon, purified graphite, or clear white diamonds) were heated

in separate tubes in a vacuum to 1000° until practically no further gas (less than 0·1 c.c. per hour) was evolved, the pump working continuously. The iron and carbon were then brought into contact, with sa little exposure to the air as possible, and again heated in a vacuum at 700°, which is below the temperature of rapid cementation, until the evolution of gas ceased. The temperature was then raised to 1000° and maintained at that temperature for several hours, the pump working continuously. In every case the results were negative; microscopic examination of the surface of the metal did not show the least trace of cementation. If, however, small quantities of gas were let into the apparatus, or if the pump was not continually worked, cementation took place, no matter what kind of carbon was used.

The adherence of carbon to iron under high pressures (3,000 atmos.) is very slight; hitherto, it has not been possible to carry out such experiments in a vacuum at high temperatures in order to ascertain if cementation is affected by the pressure.

If it be granted that carbon cannot penetrate into steel from the outside, except by means of some gaseous medium (carbon monoxide), it does not follow that the same thing holds for the diffusion of carbon to the interior of a casting or of steel. Fresh experiments in this direction are necessary. T. S. P.

Metallic Tungsten. LUDWIG WEISS (*Zeitsch. anorg. Chem.*, 1910, **65**, 279—340).—[With A. MARTIN.]—The aluminothermic reduction of wolframite is very violent, and an alloy is obtained, but by employing an insufficient quantity of aluminium, the reaction is moderated, and the product contains up to 90·66% W. A part of the iron and manganese can be removed by treatment with hydrochloric acid. It is not possible to reduce wolframite with zinc or magnesium, but heating with carbon in an arc furnace, followed by fusion with tungstic acid and calcium fluoride to remove carbon, gives a product containing only 0·24% C and 8·34% Fe.

Tungstic acid is best prepared by fusing wolframite with calcium carbonate and calcium chloride, and decomposing the product with acid. If magnesium carbonate is employed, the product contains large, red crystals of magnesium tungstate, which is not decomposed by acids. Tungstic acid may be readily electrolysed if mixed with cryolite, 250 amperes being employed at 13—14 volts. The metal is only obtained in globules, and contains 96% of tungsten. In order to raise the temperature, alumina may be added to the bath, the aluminium liberated reacting with the tungstic acid, but the product is still in a fine state of division. Experiments have also been made on the electrolysis of barium tungstate, and the reduction of calcium tungstate with aluminium. The best metal, containing 98·96% W, is obtained by fusing tungsten trisulphide with lime by means of an arc in a crucible of Acheson graphite.

[With A. STIMMELMAYR.]—Tungsten, fused in a hydrogen vacuum, is white and metallic; H 6·5—7·5, D^{20} 18·72. The malleability varies according to the heat treatment it has received. Small fragments may be hammered out. It is non-magnetic. The specific heat is 0·0358, and the heat of combustion of 1 gram is 1047 cal.

Tungsten forms coloured films, like steel, when heated in the air. Heating in oxygen converts it completely into the trioxide. Hydrochloric acid is without action; concentrated sulphuric and nitric acids and aqua regia only act slowly on the surface. Chlorine acts slowly; sulphur is without action. A mixture of nitric and hydrofluoric acids is the only reagent capable of dissolving the fused metal.

C. H. D.

Corrosion of Bronzes in Solutions of Electrolytes. FEDERICO GIOLITTI and O. CECCARELLI (*Gazzetta*, 1909, **39**, ii, 557—575).—The authors have studied the corrosion of bronzes containing various proportions of tin, and subjected to different methods of cooling by means of 80 c.c. of N/10-hydrochloric acid containing 2% of ferric chloride. The losses in weight were determined after 169 and 366 hours, the results being compared with the aid of micrographs.

It is found that two bronzes of identical composition, after subjection to different thermal treatment, may exhibit quite different powers of resistance to corroding agents; such differences correspond with structural differences (compare Curry, Abstr., 1906, ii, 756; Giolitti and Tavanti, Abstr., 1908, ii, 946). Under similar conditions, the simultaneous presence in a bronze of the two α and β solid solutions, and especially of the products of segregration of these, accelerates the corrosive action. With bronzes containing not much more than 7% of tin, the velocity of corrosion increases with the proportion of the β-solution present, no matter whether such increased proportion is due to a different composition of the alloy or to different thermal treatment, such as altered velocities of solidification and of subsequent cooling. When the proportions of α and β solutions, and of their segregation products, remain constant, the velocity of corrosion is greater when the differences of concentration of the nuclei and margins of the separate mixed crystals of the two series are greater. As such differences of concentration are observable under the microscope, the degree of resistance of a bronze to corrosion may be determined beforehand by the same means.

T. H. P.

Metallic Zirconium. LUDWIG WEISS and EUGEN NEUMANN (*Zeitsch. anorg. Chem.*, 1910, **65**, 248—278. Compare this vol., ii, 133).—Crystallised potassium zirconium fluoride is mixed with purified sodium, covered with potassium chloride, and compressed into an iron vessel. After starting the reaction with a flame, it proceeds without further heating. The finely powdered metal thus obtained, is washed with alcohol, and boiled with hydrochloric acid. If washed with water first instead of alcohol, some oxide is always formed by the action of the sodium hydroxide produced on the metal. The zirconium may be compressed to form rods, which conduct electricity well, by high pressure without the use of binding material, but only globules of metal can be obtained in this way, as the rods break when a current is passed.

A better product is obtained by reducing the double fluoride with aluminium, forming the powdered regulus into rods, and heating in a specially constructed furnace in an atmosphere of nitrogen, preferably

under reduced pressure. The metallic zirconium, containing 99·8% Zr, is white, resembling cast-iron; it has H 7—8, D^{18} 6·40, and specific heat 0·0804.

Combustion in air only takes place at a very high temperature, and the formation of the dioxide is not complete unless oxygen is used. The heat of combustion of 1 gram is 1958·7 cal. It reacts with chlorine, forming the tetrachloride. Hydrogen at a red heat forms a grey hydride, ZrH_2 (compare Winkler, Abstr., 1890, 1372). When heated in oxygen, the hydride burns to *zirconium sesquioxide*, Zr_2O_3, which is stable, and only burns slowly to the dioxide. C. H. D.

Natural Zirconium Earths. EDGAR WEDEKIND (*Ber.*, 1910, 43, 290—297. Compare Abstr., 1908, ii, 1046. [Compare Weiss and Lehmann, this vol., ii, 133]).—The author has investigated three varieties of a natural zirconium earth from São Paolo, in Brazil.

I. consisted of black, kidney-shaped masses of glassy appearance.

II. consisted of broken stones, varying in colour from dark brown to a light matt-grey; very often crystals of zirconium silicate were contained in it.

III. consisted of more or less rounded pebbles.

Analyses gave the following results:

	ZrO_2.	TiO_2.	Fe_2O_3.	SiO_2(free)	SiO_2 (combined).	Total.
I.	94·12	0·98	3·22	0·43	1·98	100·73
II.	88·29	3·09	4·07	2·38	3·38	101·22
III.	74·48	1·35	10·26	$\underbrace{\qquad\qquad}_{14·08}$		100·17

The admixed ferric oxide could be removed mechanically from I.; it then contained 98% ZrO_2, and had D 5·41.

To obtain zirconium oxide free from iron, the filtered, acid, aqueous extract of the finely-powdered mineral was mixed with ammonia until a cloudiness resulted. Powdered ammonium carbonate was added until the precipitate first formed no longer dissolved. A further equal quantity of ammonium carbonate was then added, and the solution warmed to precipitate the iron. The warming was continued until a filtered portion of the liquid gave no coloration with sulphuric acid and hydrogen peroxide. The whole was then cooled, filtered, the filtrate acidified with sulphuric acid, and warmed to expel carbon dioxide, and the zirconium hydroxide precipitated with ammonia. The hydroxide was washed by decantation, and then converted into the oxide by heating.

To prepare the zirconium tetrahalogenides directly, the finely-powdered mineral was intimately mixed with excess of magnesium powder, and the mixture heated in a current of dry hydrogen. After treatment of the resulting mass with ammonium chloride, dilute hydrochloric acid, and warm dilute potassium hydroxide respectively, in order to remove the magnesium, magnesia, iron, and silicon, the residue was dried in a current of hydrogen and then heated in a stream of either chlorine or bromine. The corresponding tetrahalogenide sublimes.

The broken stones and pebbles were found to contain carbon

dioxide, nitrogen, hydrogen, oxygen, helium, and traces of argon, the broken stones containing the most gas. The mineral has been found by Gockel to be radioactive (Abstr., 1909, ii, 956), and he concluded that thorium was present. This element has, however, not yet been detected in any of the author's specimens. T. S. P.

Physical and Chemical Properties of some Varieties of Antimony Trisulphide. VITO ZANI (*Bull. Acad. roy. Belg.*, 1909, 1169—1182. Compare Guinchant and Chrétien, Abstr., 1904, ii, 538, 568, 644).—The varieties examined were (1) the orange-red form produced by precipitation; (2) the greyish-black form obtained by heating the orange-red modification, and (3) natural stibnite.

The conclusions arrived at are (*a*) that all three forms have the formula Sb_2S_3, and (*b*) that their specific gravities are 4·1205, 4·2906, and 4·6353 respectively. The first form gradually changes into the second on heating, and determinations made in various ways agreed in indicating 217° as the temperature at which transformation to the second form occurs with the development of heat. The changes of weight observed on heating the orange-red sulphide at about 100° are not due, as generally supposed, to loss of water, but to secondary reactions involving first the absorption of oxygen, then the loss of sulphur dioxide, and the eventual production of some metallic antimony. Stibnite seems to differ from the second form only in specific gravity. T. A. H.

Mineralogical Chemistry.

Mineralogy of Franklin Furnace, New Jersey. CHARLES PALACHE (*Amer. J. Sci.*, 1910, [iv], 29, 177—187).—*Arsenopyrite*, brilliant crystals from limestone, gave anal. I (by E. C. SULLIVAN). The associated iron-pyrites contains about the same proportion of cobalt, but the associated pyrrhotite contains no cobalt and only a trace of nickel:

	Fe.	Co.	As.	S.	Total.
I.	32·48	1·16	48·72	18·80	101·16

Fluorite, pale red and granular, the matrix of franklinite grains, gave II (by G. STEIGER). The deficiency is probably fluorine, but even then there is not quite enough for the formula CaF_2:

	Ca.	Mg.	Fe.	Mn.	Al.	F.	Cl,CO_2	Total.
II.	51·21	0·24	0·27	0·09	0·18	45·85	nil	97·84

Manganosite (III, by G. Steiger) forms a granular aggregate with franklinite and zincite; the irregular grains are dark green and have a cubic cleavage, being emerald-green in thin flakes; D 5·364; formula MnO. This rare species has previously been found only in Sweden.

Gahnite, variety dysluite (IV, by W. T. SCHALLER), large crystals from Sterling Hill; D 4·56.

Franklinite (V, by W. T. Schaller), small crystals of cubo-octahedral habit and adamantine lustre, and showing a deep red colour on edges or where splintered; D 5·09.

Hetærolite (VI, by W. T. Schaller); under the microscope it is seen to be tetragonal with indistinct prismatic cleavages; D 4·85. This hitherto doubtful mineral may be described as a zinc hausmannite, ZnO,Mn_2O_3 (hausmannite being MnO,Mn_2O_3).

Pyroxenes: jeffersonite (VII, by G. Steiger) and schefferite (VIII, by W. T. Schaller).

Bementite (IX, by G. Steiger) is orthorhombic with three pinacoidal cleavages. The water is expelled only at a red-heat, and the formula $H_6Mn_5(SiO_4)_4$ shows a relation to tephroite ($Mn_8Si_4O_{16}$).

Friedelite (X, by W. T. Schaller), scales and indistinct, tabular, rhombohedral crystals. Formula $H_9(MnCl)Mn_7(SiO_4)_6$, or, perhaps, $H_{20}(MnCl)Mn_{14}Si_{12}O_{49}$.

Vesuvianite, variety cyprine (XI, by G. Steiger), bluish-green, fibrous; D 3·451; formula $H_8(Al,Fe)_6Ca_{12}Si_{10}O_{45}$.

Cuspidine (XII, by C. H. WARREN), glassy, white, crystal fragments; D 2·965—2·989; formula $Ca_2Si(O,F_2)_4$. This species has hitherto been known only from Vesuvius.

	SiO_2.	Al_2O_3	Fe_2O_3.	FeO.	MnO.	MnO_2.	ZnO.	CaO.	MgO.	H_2O (105°).	H_2O (>105°).	F.	Total (less O for F.)
III.	—	—	0·26		94·59	1·30	3·41	—	0·11	0·38	0·40	—	100·45
IV.	1·47	47·27	9·90	—	0·93	—	37·10	1·01	1·09	1·21		—	100·36*
V.	—	—	66·58	—	9·96	—	20·77	0·43	0·34	0·71		—	99·51†
VI.	1·71	—	0·77	—	60·44		33 43	—	—	2·47	1·42	—	100 24
VII.	49·03	0·86	4·22	3·95	7·91	—	7·14	19·88	5·81	0·60	0·70	—	100·14
VIII.	49·80	0·26	1·46	1·61	9·69	—	trace	21·07	12·35	1·55	1·31	0·31	99·80‡
IX.	38·36	0·96	0 71	4·94	39·22	—	2 93	0·62	3·35	0 60	8 01	—	99·70
X.	34·69	—	—	1·45	48·00	—	1·05	0·63	0·98	1·94	9·08	—	100·48§
XI.	36·41	17·35	1·86		1·75	—	1·74	33·21	1·38	0·24	3·51	0·36	100·06‖
XII.	32·36	—	—	—	0 71	—	—	61·37	—	—	—	9·05	100·43¶

* Including CO_2, 0·38. † State of oxidation of iron and manganese not known. ‡ Including Na_2O, 0·9; CO_2, 0·43. § Including Cl, 3·43. ‖ Including CuO, 1·85; PbO, trace; Na_2O, 0·44; K_2O, 0·50. ¶ Including Na_2O, 0·48; K_2O, 0·27.

Crystallographic descriptions are also given of zincite ($a:c = 1:1·5870$); nasonite (hexagonal, $a:c = 1:1·3167$); glaucochroite ($a:b:c = 0·4409:1:0·5808$); willemite ($a:c = 1:0·6612$); datolite; humite, and leucophœnicite ($a:b:c = 1·1045:1:2·3155$; $\beta = 76°44'$).

Ninety-three species of minerals are recorded from this locality, several of them now for the first time. L. J. S.

Bismite. WALDEMAR T. SCHALLER and FREDERICK L. RANSOME (*Amer. J. Sci.*, 1910, [iv], **29**, 173—176).—Bismite occurs in the oxidised zone in several mines in the Goldfield district of Nevada. It has the form of minute, pearly scales, with a brilliant, almost metallic lustre and a silvery whiteness. It encrusts the cavity-walls of spongy limonite and quartz, and has been derived by the alteration of bismuthinite (Bi_2S_3). Under the microscope the thin, colourless scales show a hexagonal outline with triangular markings on the base,

and a negative uniaxial interference-figure; there is a perfect basal cleavage. The crystals are therefore rhombohedral, $a : c = 1 : 0{\cdot}5775$. (Artificial crystals of bismuth trioxide are orthorhombic.) Analysis of material mixed with much gangue (mainly quartz) gave:

Bi_2O_3.	H_2O (loss on ignition).	Fe_2O_3.	Insoluble in HCl.	Total.
17·04	3·96	0·36	78·94	100·30

These results indicate that the crystals are either bismite (Bi_2O_3) or a hydrous bismuth oxide. If the latter be the case, the mineral is a new species (providing, of course, that Bi_2O_3 is the correct formula for bismite or bismuth ochre). L. J. S.

Variety of Cobaltiferous Calcite from Capo Calamita, Elba. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 91—92).—The author describes a sample of vivid red calcite occurring in crystalline masses on a limonitic and partly magnetitic rock. It is slightly harder than normal calcite, has D 2·75, and has the following composition:

CaO.	CoO.	FeO.	MgO.	MnO.	CO_2.	Total.
54·41	1·27	0·15	0·27	trace	43·55	99·65

which corresponds with: $CaCO_3$, 97·16; $CoCO_3$, 2·02; $FeCO_3$, 0·24, and $MgCO_3$, 0·56. The name *cobalto-calcite* is given to the mineral.
T. H. P.

The Plumboniobite Earths. OTTO HAUSER (*Ber.*, 1910, **43**, 417—419).—Spectroscopic examination of the plumboniobite described in a previous communication (Abstr., 1909, ii, 676) shows that the formula therein given must be modified to $R_2''Cb_2O_7,R_4'''(Cb_2O_7)_3$, where R″ represents Pb, Fe, UO, and Ca, and R‴ represents Y, Gd, Yb, and Al. T. S. P.

A Uranium Ore from German East Africa. WILLY MARCKWALD (*Landw. Jahrb.*, 1909, **38**, *Erganz. band V.*, 423—425, *Thiel Festschrift*).—An account of the methods employed, with the tabulated results of the analysis of a mineral found in German East Africa containing 80—90% uranium oxides ($UO_3 = 45\%$, $UO_2 = 39\%$) and 7—8% lead oxide (PbO). F. M. G. M.

Minerals from the Pegmatites of Madagascar. LOUIS DUPARC, R. SABOT, and M. WUNDER (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 62—71).—The pegmatite veins in the neighbourhood of Antsirabé are intrusive into quartzites and cipolins; they consist mainly of quartz and orthoclase, with some mica and various accessory minerals (tourmaline, beryl, spodumene, garnet, etc.) in large crystals of gem-quality. Usually the pegmatite is much decomposed.

Spessartite (anal. I), of gem-quality and honey-yellow or brown in colour, occurs in pegmatite at Tsilaisina; refractive index (Na), 1·79980.

Cordierite (anal. II) was found as irregular fragments in the

micaceous quartzite of the Ibity range; refractive indices, $\alpha = 1·53958$, $\beta = 1·54516$, $\gamma = 1·54853$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	TiO_2.	Loss on ignition.	Total.	Sp. gr.
I.	35·76	21·06	1·78	—	39·40	1·23	0·46	0·10	—	99·79	4·0586
II.	49·05	33·08	0·83	4·38	—	—	11·04	—	1·64	100·02	2·5933

Crystallographic descriptions are also given of large zoned (red and brown) crystals of tourmaline from several localities. These crystals are optically biaxial with a small axial angle; refractive indices are given. L. J. S.

Chemico-physical Investigations and Analysis of the Iron- and Arsenic-containing Water of Roncegno. RAFFAELO NASINI, MARIO GIACOMO LEVI, and F. AGENO (*Gazzetta*, 1909, 39, ii, 481—512).—The results of the authors' chemico-physical measurements on this water are as follows: D_4^{25} 1·00293; freezing point, $-0·10°$; osmotic pressure, $P = 1·205$ atmos.; specific electrical conductivity, $K_{25} = 0·00453$; radioactivity, intensity of saturation current, $I = 167·8 \times 10^{-15}$ amperes. The large amount of arsenic renders the full analysis interesting. The dissolved matter, in grams per litre, is as follows:

CuO.	FeO.	Fe_2O_3.	Al_2O_3.	MnO.	NiO.	CoO.
0·01463	0·01006	1·21230	0·26670	0·01952	0·00325	0·00295
CaO.	MgO.	Na_2O.	K_2O.	SO_3.	SiO_2.	P_2O_5.
0·58919	0·11400	0·01109	0·00325	3·53880	0·13160	0·00740

As_2O_3.	As_2O_5.	NH_3.	Cl.	Li_2O.	TiO_2.	Residue at 100°.	Residue at 180°.
0·00350	0·05744	0·00027	0·00007	Trace.	Trace.	7·1610	6·5560

T. H. P.

Physiological Chemistry.

Narcosis and Want of Oxygen. II. The Effect of Deprivation of Oxygen on the Resting Current of Frog's Skin. G. MANSFIELD (*Pflüger's Archiv*, 1910, **131**, 457—464).—Alcock has shown that narcotics of the fatty series abolish or lessen the secretion current of the frog's skin, but only if the narcotic is applied to its outer surface. Deprivation of oxygen acts in exactly the same way, and this is considered to support the theory that the narcotics in question produce their effects by lessening the supply of oxygen to the cell lipoids. W. D. H.

Gaseous Metabolism of the Dog's Heart during Vagus Inhibition. J. M. WOLFSOHN and L. W. KETRON (*Proc. Amer. physiol. Soc.*, 1909, 25—26; *Amer. J. Physiol.*, **25**).—The gases of the blood were analysed by the use of the mercury pump, and Barcroft and

Dixon's results were confirmed that vagus inhibition lessens the oxygen absorbed and the carbon dioxide produced, the latter being the more marked. W. D. H.

The Inhibition of Soap Hæmolysis. WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1910, **62**, 145—155).—The hæmolysis produced by soaps is inhibited by cholesterol and also by two other lipoids, kephalin and cerebron. Sodium stearate and palmitate, which possess hæmolytic properties, increase the hæmolysis produced by sodium oleate. Alcoholic extracts of organs inhibit hæmolysis produced by soaps and by saponin. Dissolved red corpuscles protect other red cells from the solvent action, probably by the fact that lipoids are liberated. W. D. H.

Observations on the Inhibitory Influence Exerted by Hypertonic Saline Solutions and Calcium Chloride Solutions on the Action of Specific Hæmolysins with Suggestions as to the Therapy of Blackwater Fever. W. D. SUTHERLAND and DAVID MCCAY (*Bio-Chem. J.*, 1910, **5**, 1—22).—In blackwater fever the corpuscles are more vulnerable than in the normal state, and the liberation of hæmoglobin is due to a hæmolysin. Salts which decrease the number of inorganic ions in the plasma are recommended, for such salts to a large extent inhibit hæmolysis *in vitro*. The intravenous injection of a mixture of sodium chloride and calcium chloride is recommended. W. D. H.

Action of Biotoxin on Blood. FRANCESCO MARINO-ZUCO and L GIUGANINO (*Gazzetta*, 1909, **39**, ii, 586—616).—Further experiments on the toxin previously described (Abstr., 1904, ii, 754) give the following results. The biotoxin, as the authors term it, has an energetic poisoning effect on the blood, its action, which can be followed by means of the spectroscope, being as follows. The oxyhæmoglobin is resolved by the action of the enzyme into two principal substances, one of which has a protein character and contains all the iron of the hæmoglobin, the other being a non-protein pigment which is apparently analogous to the colouring matter of the bile and exhibits a spectrum characterised by a band in the red, $\lambda = 650—632$, and another between the blue and green, $\lambda = 520—490$. This action on the blood pigment is so sensitive that, by means of the spectroscope, the presence of one five-millionth (1/5,000,000) of the biotoxin in 1 c.c of 10% defibrinated blood solution can be recognised. In small proportions the biotoxin occurs in circulating blood, its presence being demonstrated, not only by direct extraction, but also by the changes taking place in sterilised blood solutions when these are maintained for three months at 40—41° (the optimum temperature of the toxin) or for a longer period at the ordinary temperature. T. H. P.

Influence of Alcohol on Metabolism. LAFAYETTE B. MENDEL and WARREN W. HILDITCH (*Proc. Amer. physiol. Soc.*, 1909, 11; *Amer. J. Physiol.*, **25**).—The most marked result of alcohol as revealed by urinary analysis is to increase the amount of purine

substances. "Protein sparing" so frequently observed before was also shown to occur. The paucity of the results indicates that the body can maintain its catabolic functions along normal channels, despite the interference of toxic agents, a factor of safety being present. In the more marked conditions of alcoholism, conjugated glycuronates may be excreted both in men and animals: these disappear with the cessation of the intake of alcohol.

W. D. H.

Relation of Pancreas to Sugar Metabolism. WESLEY M. BALDWIN (*Proc. Amer. physiol. Soc.*, 1909, 21—22; *Amer. J. Physiol.*, 25).—Experiments with the muscles and pancreas of cats, frozen solid by liquid air and then powdered, show that when extracts are made, the presence of the pancreas increases glycolysis in an alkaline medium, and thus the original statements of O. Cohnheim are confirmed. W. D. H.

Digestion of Inulin. H. BIERRY (*Compt. rend.*, 1910, **150**, 116—118).—In the higher animals, transformation of inulin is effected by the hydrochloric acid of the gastric juice, and is not due to the presence of a soluble pancreatic ferment. The pancreatic juice of dogs is incapable of effecting hydrolysis. The gastro-intestinal secretion of *Helix pomatia*, however, slowly hydrolyses inulin with formation of lævulose. W. O. W.

Effects of Carbohydrates on the Artificial Digestion of Casein. NELLIE E. GOLDTHWAITE (*J. Biol. Chem.*, 1910, **7**, 69—82). —Carbohydrates retard the digestion of caseinogen *in vitro*, in proportion to the amount added. W. D. H.

Chemical and Bacteriological Study of Fresh Eggs. MARY E. PENNINGTON (*J. Biol. Chem.*, 1910, **7**, 109—132).—In fifty-seven eggs, seven only were sterile; in the remainder, bacteria, of which thirty-six varieties were identified, were present both in white and yolk. The chemical data relate mainly to nitrogenous compounds in both white and yolk—nitrogen coagulable by heat, in filtrate, in tannic acid precipitate, etc. These details are given in numerous tables. W. D. H.

The Phosphorus-content of Growing Dogs. ALEXANDER LIPSCHÜTZ (*Arch. exp. Path. Pharm.*, 1910, **62**, 210—243).—In growing dogs, restriction of the diet to rice and white of egg leads to a relative "phosphorus hunger," the body containing only from one-sixth to one-fifteenth of the normal amount of phosphorus. This diet, poor as it is in phosphorus, leads to changes in the skeletal system similar to those found in the bones in "Barlow's disease," and to a slower rate of growth than normal. W. D. H.

Irregularities of the Mammalian Heart under Aconitine. ARTHUR R. CUSHNY (*Heart*, 1909, **1**, 1—22).—From experiments on dogs, in which aconitine in 0·05 mg. doses was injected intravenously, it was found that several forms of cardiac irregularity could be pro-

duced, among which impaired conduction through the auriculo-ventricular bundle may be mentioned. Aconitine has a greater tendency to cause pulsus alternans than most other poisons.

W. D. H.

Influence of the Pancreas on the Glycolytic Power of Muscle. G. C. E. SIMPSON (*Bio-Chem. J.*, 1910, **5**, 126—142).—By incubation of muscle juice or extract, especially in the presence of pancreatic juice, large amounts of reducing substances are formed, possibly from glycogen, but more largely from autolytic or tryptic digestion of the muscle plasma. The nature of these substances has still to be investigated. The difficulty of maintaining asepsis is, however, almost insuperable, and the difficulty of estimating sugar in the presence of large amounts of proteins leads to great experimental error. So far as observations are possible under these limitations, the glycolysis obtained by the combined action of pancreatic and muscle juices is believed to be not, as a rule, greater than the sum of the actions of the constituents of the mixture. W. D. H.

The Silicic Acid in Whartonian Jelly. HUGO SCHULZ (*Pflüger's Archiv*, 1910, **131**, 447—456).—Frauenberger (Abstr., 1908, ii, 969) having thrown doubt on the statements of the author regarding silicic acid in the Whartonian jelly of the human umbilical cord, the experiments in question have been repeated, and the results are practically the same as in the previous investigation (Abstr., 1902, ii, 275), namely, that the jelly contains 4% of ash, not 11·6% as stated by Frauenberger, and that 1 kilogram of the dried jelly contains 0·24 gram of silica. W. D. H.

The Parent Substance of Glycogen. EDUARD PFLÜGER and PETER JUNKERSDORF. **Postscript.** EDUARD PFLÜGER. **Influence of Phloridzin on the Sugar in the Blood.** PETER JUNKERSDORF. **Estimation of Glycogen in the Tortoise's Liver.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1910, **131**, 201—301, 302—305, 306—313, 314—316).—The first paper contains protocols of over 150 experiments on dogs. The liver was rendered almost free from glycogen by means of phloridzin and inanition; but twenty-four hours later, if no more phloridzin is given, the liver may contain as much as 3% of glycogen; the mean percentage in thirty-eight experiments was 1·1%. If cod's flesh is given, the percentage rises enormously, and the conclusion is drawn that this is not a "sparing" phenomenon, neither is the glycogen derived from fat, but from protein. In fact, this is regarded as the first absolute proof of the origin of carbohydrate from protein. Excessive doses of protein food do not increase the percentage of glycogen so much as moderate doses.

In the postscript, a few experiments given seem to indicate that glycine may act as a parent substance of glycogen, but these are to be repeated on a larger scale.

The third paper confirms the previously well-known fact that in phloridzin diabetes the amount of sugar in the blood is not higher than normal: it may be lower.

Pflüger's method of estimating glycogen has been tested already in thousands of cases; the tortoise's liver, however, does not lend itself, for certain unexplained reasons, to the method; in this case, therefore, reliance has to be placed on a previous method which is not so exact.

W. D. H.

Physiology of Lymph. X. The Comparative Electrical Conductivity of Lymph and Serum, and its Bearing on Theories of Lymph Formation. A. B. LUCKHARDT (*Amer. J. Physiol.*, 1910, **25**, 345—353).—Several observers have stated that lymph contains more chlorides than serum; this is confirmed by the electrical conductivity method. The serum is certainly richer in protein than lymph, but the increase of protein (as shown by experiments on white of egg) is inadequate to explain the lesser conductivity of the former fluid. Fat droplets in the chyl depress the conductivity of lymph. A 10% increase in the amount of sodium chloride in physiological saline solution produces an effect on conductivity comparable to that seen in comparing lymph and serum. The excess of chlorides awaits explanation, and is not compatible with purely mechanical theories of lymph formation. W. D. H.

Physiology of Lymph. XI. The Fractional Coagulation of Lymph. HERBERT O. LUSSKY (*Amer. J. Physiol.*, 1910, **25**, 354—366).—Lymph may coagulate in successive crops of fibrin; this will depend on the amount of thrombin present. In lymph the conversion of prothrombin into thrombin by calcium appears to occur very slowly. A small yield of fibrin with a small amount of ferment in a given time is no proof that thrombin is not an enzyme, as Rettger (Abstr., 1909, ii, 680) considers. The time factor was neglected by this observer; after the lapse of a longer time, as much fibrin may be formed as in other specimens is formed by larger amounts of the enzyme in a shorter time. W. D. H.

Presence in Cow's Milk of an Anæroxydase and a Catalase. J. SARTHOU (*Compt. rend.*, 1910, **150**, 119—121. Compare this vol., ii, 57).—Polemical against Bordas and Touplain (*loc. cit.*). The author quotes the results of experiments which appear to show that the catalytic actions brought about by filtered milk are due, not to casein, but to lactic ferments. W. O. W.

Reactions of Curdled Milk due to the Colloidal State. FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1910, **150**, 341—343. Compare this vol., ii, 57).—The authors consider that the reactions of curdled milk, hitherto attributed to the presence of enzymes, may be explained by the colloidal state of the casein. Colloidal solutions of ferrous oxalate or ferric lactate are found to give all the catalytic reactions of curdled milk, decomposing hydrogen peroxide, for example, and developing a blue coloration with *p*-phenylenediamine. Curdled milk which has been heated to 110° and cooled gives no reaction with these substances; if, however, the casein is brought to a very finely-divided state by allowing a jet of the liquid under a pressure

of 300 atmospheres to impinge on an agate plate, it becomes endowed with marked catalytic properties. W. O. W.

The Phosphorus in Fæces. ALEXANDER LIPSCHÜTZ (*Arch. exp. Path. Pharm.*, 1910, **62**, 244—252).—The normal fæces of the growing animal (dog and man) are poorer in phosphorus than in the adult condition. W. D. H.

The Degradation of Fatty Acids in Diabetes mellitus. JULIUS BAER and LEON BLUM (*Arch. exp. Path. Pharm.*, 1910, **62**, 129—138. Compare Abstr,, 1908, ii, 1057).—It has been shown previously by the authors that the administration of butyric acid, hexoic acid, β-methylbutyric acid, β-ethylbutyric acid, leucine, phenylalanine, and tyrosine to diabetics causes an increase of β-hydroxybutyric acid, and members of that group in the body that constitutes acidosis. Stress is laid on the importance of the β-position in the substances given. The present research relates mainly to leucine; *d*-leucine produces no effect, but the naturally occurring *l*-leucine is effective in the direction above indicated. Embden states that by perfusing the liver with *d*-leucine, acetone formation is observed, and that this does not occur with *l*-leucine. These experiments were repeated, but no marked difference could be observed between the two isomerides.

W. D. H.

Formation of Glycogen in the Liver of Tortoises with Pancreatic Diabetes. M. NISHI (*Arch. exp. Path. Pharm.*, 1910, **62**, 170—179).—The blood of normal tortoises contains no reducing substance; total extirpation of the pancreas leads to intense glycæmia and glycosuria; in this condition perfusion of the liver with a solution of dextrose leads to glycogen formation there as in normal animals.

W. D. H.

The Production of Sugar from Amino-acids. A. I. RINGER and GRAHAM LUSK (*Proc. Amer. physiol. Soc.*, 1909, 19; *Amer. J. Physiol.*, **25**).—Both glycine and alanine administered to dogs suffering from phloridzin glycosuria are completely converted into sugar; and three of the four carbon atoms in aspartic acid, and three of the five in glutamic acid, are similarly convertable into dextrose.

W. D. H.

Phloridzin Glycocholia. R. T. WOODYATT (*J. Biol. Chem.*, 1910, **7**, 133—136).—The administration of phloridzin leads to presence of sugar, not only in the urine, but also in the bile; its action is, therefore, not confined to the kidneys. W. D. H.

Acapnia and Shock. V. Failure of Respiration after Intense Pain. YANDÊLL HENDERSON (*Amer J. Physiol.*, 1910, **25**, 385—402. Compare this vol., ii, 137).—A continuation of work along the same lines as in previous papers. The point specially insisted on is that serious and even fatal apnœa may be a result of intense pain, and a case in support of this view, in a man, is recorded.

W. D. H.

Antagonistic Action of Barium and Magnesium. DON R. JOSEPH and SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1909, 17—18; *Amer. J. Physiol.*, 25).—In rabbits, 1·2 grams of magnesium sulphate per kilo. of body-weight are fatal. It has been previously shown that these effects are antagonised by calcium salts. The effect on the respiration is also antagonised by barium salts, although the animal remains anæsthetised and otherwise paralysed. The same dose of barium chloride alone is fatal, so that the toxic effects of barium are antagonised by magnesium. W. D. H.

The Increase of Susceptibility to Adrenaline Produced by Cocaine. ALFRED FRÖHLICH and OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1910, **62**, 159—169).—Small inactive doses of cocaine increase markedly the intensity and duration of the effects of adrenaline on the blood-vessels, eye, and bladder. The combination of the two is therefore recommended for therapeutic use. W. D. H.

Fate of Sodium Benzoate in the Human Organism. HENRY D. DAKIN (*J. Biol. Chem.*, 1910, **7**, 103—108).—Sodium benzoate in doses of 5 to 10 grams a day for two or three days is wholly eliminated in the urine as hippuric acid. The increase of glycuronic acid derivatives is trifling. These results confirm those of Lewinski (Abstr., 1908, ii, 518; 1909, ii, 820), and are in opposition to those of Brugsch and Tsuchiya (*Zeitsch. expt. Path. Ther.*, 1909, **5**, 937). An improved method of hippuric acid estimation is described.
W. D. H.

The Action of Ether on the Circulation. E. H. EMBLEY (*Bio-Chem. J.*, 1910, **5**, 79—93).—Ether administered with plenty of air lowers the blood-pressure; in high concentration it paralyses the heart muscle. It stimulates the inhibitory mechanism of the heart, and relaxes the arterioles. It is in every way safer than chloroform.
W. D. H.

The Chemistry and Bio-chemical and Physiological Properties of a Sapo-glucoside obtained from the Seeds of Bassia longifolia (Mowrah Seeds). BENJAMIN MOORE, MISS S. C. M. SOWTON, F. W. BAKER-YOUNG, and T. ARTHUR WEBSTER (*Bio-Chem. J.*, 1910, **5**, 94—125).—The sapo-glucoside in question is named *mowrin*. Directions for its isolation are given; on hydrolysis, it yields *mowric acid*, furfuraldehyde, and dextrose. It is very toxic, and workers with Mowrah meal suffer from virulent cellulitis of the hands and feet. Details are given *inter alia* of its hæmolytic action, and of its action on the heart; in the latter relation it resembles drugs of the digitalis group. W. D. H.

Comparative Action of Stovaine and Cocaine as Measured by their Direct Effect on the Contractility of Isolated Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. Roy. Soc.*, 1910, *B*, **82**, 147—151).—Stovaine, methylstovaine, and cocaine have approximately equal affinity values as measured by the methyl-orange

and borax precipitation methods. Measured by Waller's method, the toxicities of these drugs to plain muscle are also equal. G. S. W.

Toxicity of Thallium Salts. ROBERT E. SWAIN and W. G. BATEMAN (*J. Biol. Chem.*, 1910, **7**, 137—151).—The toxicity of thallium salts has been a matter of divergence of opinion. The present experiments on numerous species of animals show that it is among the most toxic of the elements. The symptoms closely resemble those of uræmic poisoning, but the kidneys so far examined show no very severe changes. W. D. H.

Mercury and Hirudin. MLLE. GUSTAVA PRUSSAK (*Arch. exp. Path. Pharm*, 1910, **62**, 201—209).—The toxic action of mercury (given as sublimate) is much increased by the administration of hirudin; the minimal lethal dose of the former is thus lessened. The same symptoms and pathological appearances occur as when the blood is not rendered incoagulable by hirudin. W. D. H.

Cobra Poison and Hæmolysis. III. IVAR BANG (*Biochem. Zeitsch.*, 1910, **23**, 463—498. Compare Abstr., 1909, ii, 681).—Although pure lecithin has no influence on the hæmolysis produced by cobra venom, it is shown that commercial lecithin acts as an activator under a number of different experimental conditions. This is explained by the hypothesis that the membrane of the corpuscles is rendered more permeable to salts, especially to their acid constituents, the lecithin combining with the alkali. It is further supposed that there are two receptors, and that the poison reacts with the second receptor in the presence of lecithin; it is this which renders the lipoid membrane permeable. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Assimilation of Carbon by Bacteria which Oxidise Hydrogen. A. J. LEBEDEFF (*Ber. deut. bot. Ges.*, 1910, **27**, 598—602).—The development of the microbe employed in a solution containing minerals and nitrate is coincident with an absorption of carbon dioxide, hydrogen, and oxygen, and a slight liberation of free nitrogen. The average result of about fifty experiments showed that for 100 c.c. of carbon dioxide used, 500 to 1500 c.c. of hydrogen were oxidised. The oxidation of hydrogen takes place, however, when carbon dioxide is absent, the hydrogen and oxygen being absorbed in the relation $H_2 : O_2 = 2$.

In the autotrophic assimilation of carbon dioxide, the volume of oxygen liberated is equal to that of the carbon dioxide. The process is the same as that which takes place in green plants. In complete absence of free oxygen the process is slow. N. H. J. M.

Cellulose as Source of Energy in the Assimilation of Atmospheric Nitrogen. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1910, ii, **26**, 222—227).—*Clostridium*, in conjunction with organisms which decompose cellulose, gives better results with cellulose than *Clostridium* alone with dextrose, sucrose, starch, lactose, or mannitol. The amount of nitrogen fixed depends on the concentration, being higher, per gram of substance fermented, the lower the concentration. With *Clostridium* + methane fermentation, the amounts of nitrogen fixed were 10·4 and 5·4 mg. per gram with 0·5 and 1%, whilst with *Clostridium* + hydrogen fermentation the amounts were 8·3 and 7·7 mg. respectively. *Azotobacter* + methane fermentation gave 4·5 mg. nitrogen per gram (0·5% cellulose). N. H. J. M.

Agar-Agar as Source of Energy in the Assimilation of Atmospheric Nitrogen. HANS PRINGSHEIM and ERNST PRINGSHEIM (*Centr. Bakt. Par.*, 1910, ii, 227—231).—In a solution containing 0·2% agar and 0·04% dextrose inoculated with *Bacillus gelaticus* + *Clostridium Americanum*, 26 6 mg. of nitrogen were assimilated per gram of agar, whilst with a similar solution containing 0·005% of ammonium phosphate instead of dextrose, the amount of nitrogen fixed was 15·4 mg. per gram. Two experiments, in which solutions containing (1) 0·5% agar and 0·1% mannitol, and (2) the same proportion of agar and 0·04% mannitol, were inoculated with *B. gelaticus* + *Azotobacter chroococcum* resulted in the fixation of 14 and 6·8 mg. nitrogen respectively.

The results are of interest as they account for the origin of the nitrogen required by the vegetable and animal organisms in the sea. Benecke and Keutner (*Ber. deut. bot. Ges.*, 1903, **21**, 333) showed that both *Azotobacter* and *Clostridium* occur in sea-water, and the present results indicate that the agar present in the red and brown Algæ is rendered available as source of energy with the help of *Bacillus gelaticus.* N. H. J. M.

Ammonia and Nitrates as Sources of Nitrogen for Mould Fungi. G. RITTER (*Ber. deut. bot. Ges.*, 1910, **27**, 582—588).—The assimilation of ammonia by mould fungi is the more complete the weaker, and less poisonous, the acid liberated from the salt, and the development of the fungi on nutritive solutions containing ammonium salts is in direct proportion to their power of resisting the action of free acids.

Aspergillus niger and *Rhizopus nigricans* liberate considerably more acid than the amount which permits the germination of their spores, whilst with submerged fungi, such as the *Mucoraceae*, the amount of acid produced tends to be below the limit.

Aspergillus glaucus, *Mucor racemosus*, and *Cladosporium herbarum*, which are termed "nitrate" fungi (Laurent, *Ann. Inst. Pasteur*, 1888, **2**, 593, and 1889, **3**, 362), develop at least as well, and in part better, when supplied with ammonium salts as with nitrates. *Rhizopus nigricans*, *Mucor mucedo*, and *Thamnidium elegans* do not assimilate nitrates appreciably. N. H. J. M.

Production and Utilisation of Nitrous Oxide by Bacteria. BRUNO TACKE (*Centr. Bakt. Par.*, 1910, ii, **26**, 236. Compare Beyerinck and Minkmann, *ibid.*, **25**, 30).—The author refers to a previous paper (*Landw. Jahrb.*, 1887, **16**, 917) in which he showed the production of considerable amounts of nitrous oxide in denitrification experiments.

Nitric oxide may also be produced in considerable quantity. An experiment in which beet was fermented in a vacuum yielded so much nitric oxide in eight or ten days that red fumes were seen on opening the vessel. N. H. J. M.

Influence of Depth of Cultivation on Soil Bacteria and their Activities. WALTER E. KING and CHARLES J. T. DORYLAND (*Kansas State Agric. Coll. Exper. Stat. Bul.*, **161**, 1909).—Two plots, each 42 feet square, the one a silt loam, and the other a fine sand, were divided into six sub-plots, the soil of which was stirred to the depth of two, four, six, eight, and ten inches respectively, one sub-plot being left undisturbed. Samples were frequently taken, and the number of bacteria determined. The temperature of the soil was recorded, and the amount of moisture in the first twelve inches of soil determined each time.

The results showed that deep ploughing (eight to ten inches) increased the number of bacteria in both soils. It also increased the production of ammonia in the soil, whilst denitrification was decreased. The maximum number of bacteria was found within the fifth and sixth inches.

An excess of moisture in the soil reduces the number and diminishes the activity of the bacteria. There are, however, more or less regular periods of increased and diminished bacterial life and activity, to some extent independent of moisture and temperature, and due, perhaps, to the presence of bacterial by-products.

N. H. J. M.

New Theory of Alcoholic Fermentation. R. KUSSEROW (*Centr. Bakt. Par.*, 1910, ii, **26**, 184—187).—The theory is essentially as follows: The yeast, requiring oxygen, reduces the sugar to a hexahydric alcohol, which decomposes into ethyl alcohol, carbon dioxide, and hydrogen. The nascent hydrogen causes a further reduction of sugar, followed by the decomposition of the alcohol, and this continues until the sugar is used up or until the fermentation is stopped by the oxidation of the hydrogen.

Fermentation is therefore first brought about by the reducing action of the living yeast cell, or by similarly acting organisms, whilst its continuation is purely chemical, depending on the production of hydrogen. N. H. J. M.

Action of Ultra-violet Light on Wine During Fermentation. CHARLES MAURAIN and G. WARCOLLIER (*Compt. rend.*, 1910, **150**, 343—344. Compare Abstr., 1909, ii, 752).—The sterilisation of white wine under the action of ultra-violet light takes place with greater rapidity than in the case of cider previously studied. Thus a

layer of wine, 1·7 mm. in thickness, is sterilised in thirty to sixty seconds when exposed at 4 cm. from a quartz-mercury lamp, whilst under the same conditions cider requires about fifteen minutes.

W. O. W.

Causes Favouring the Formation of Acetaldehyde in Wine. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1910, [iv], 7, 71—78).—In previous papers (Abstr., 1909, ii, 429, 606, 607) the author has shown that wine contains acetaldehyde, and has directed attention to the important influence of this constituent in the "ageing," "yellowing," and other changes which take place in stored wine. In the present paper the conditions under which aldehyde is formed are considered.

It is shown that wine agitated with air, or merely exposed to air, produces acetaldehyde more rapidly than an aqueous solution of alcohol of the same strength. The amount formed varies with the temperature and the nature of the containing vessel. Old wines contain more aldehyde than new ones. The amount of aldehyde is increased by the presence of yeast and other micro-organisms and by the addition of oxidising agents, and its formation is accelerated by iron (Abstr., 1909, ii, 429).

T. A. H.

Germicidal Action of Metals and its Relation to the Production of Peroxide of Hydrogen. ALLAN C. RANKIN (*Proc. Roy. Soc.*, 1910, *B*, 82, 78—87. Compare Barnes and Shearer, Abstr., 1908, ii, 344, 829).—The capacity of the pure metals, zinc, aluminium, and copper to destroy *Bacillus coli* suspended in an alkaline tap-water is associated with the coincident presence of oxygen and the solution of minute traces of the metals.

The simultaneous liberation of hydrogen peroxide in the case of the first two metals, although easily recognised, is not sufficient in amount to explain the germicidal action. In the case of copper no formation of hydrogen peroxide could be detected.

G. S. W.

Disinfection by the Incomplete Combustion of Straw. AUGUSTE TRILLAT (*Compt. rend.*, 1910, 150, 339—341).—The fumes produced during the limited combustion of straw in air owe their disinfectant properties to the presence of aldehydes and phenolic compounds. These appear to be produced by catalytic oxidation of alcohols, acetic acid, acraldehyde, etc., in presence of finely-divided carbon. Formaldehyde, which has been recognised by its action on dimethylaniline, is formed to the extent of 0·002 to 2 grams per kilo. of straw. The results of experiments on bacteria are given, from which it appears that the germicidal action is well marked with pathogenic organisms, such as *Bacillus coli communis*, but that the fumes are less efficacious in the case of more resisting bacteria.

W. O. W.

Action of Aqueous Solutions of Electrolytes on Germination. HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1909, 1076—1118).—The first of two papers on the influence exerted by electrolytes on the

germination of seeds. Wheat was used for the experiments. The chief conclusions arrived at are as follows: The osmotic pressure of the solutions employed ($N/10$ to $N/1000$) did not influence the germination; the greater difference between the effects on germination of $N/10$ and $N/100$ solutions than between the effects of $N/100$ and $N/1000$ solutions is due not to greater differences in osmotic pressures of the solutions, but to greater differences in ionisation; the formation of root hairs is favoured by the presence of $-NO_3$ ions; the experimental evidence does not support the view that the growth of cells is due to the osmotic pressure of cell sap.

Wheat grains of about equal size were soaked in water for twenty-four hours, and then placed for a certain time on muslin lying in a solution of the electrolyte. At the end of this time the seedlings were removed, and the progress of germination determined by measuring (1) length of first leaf; (2) length of radicle; (3) average weight of seedling. The last of these factors for single electrolytes is given in the following table:

Concentration.	NaCl.	KCl.	KNO_3.	KHO.	$Ca(NO_3)_2$.
$N/10$	0·133	0·130	0·146	—	0·126 gram
$N/100$	0·216	0·235	0·291	—	0·152 ,,
$N/1000$	0·211	0·214	0·315	0·226	0·221 ,,

$N/100$ solutions of potassium chloride and potassium nitrate are each more favourable to germination than mixtures of such solutions, whilst mixtures of sodium nitrate and potassium nitrate solutions ($N/100$) are more favourable than those of either salt alone. Previous investigations on the antagonistic action of sodium chloride to other salts (compare Coupin, Abstr., 1900, ii, 236; Micheels, Abstr., 1907, ii, 124; Osterhout, this vol., ii, 62) as regards their influence on germination are extended, and the same action is shown to occur with strontium chloride, zinc sulphate, and barium chloride. T. A. H.

The Changes Taking Place in the Composition of Fruits which Ripen after being Gathered. RICHARD OTTO and W. D. KOOPER (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 10—13).—Results of analyses are given showing the changes which take place in the chemical composition of certain fruits (*Prunus spinosa*, etc.) when the latter are allowed to ripen (nachreifen) after being gathered. It was found that the lævulose increased from 14·44 to 21·00%, whilst the dextrose decreased from 16·04 to 10·75%, these results being calculated on the dry substance. The total acidity (as malic acid) decreased from 9·17 to 6·56%, and the tannin from 9·45 to 6·82%. The decrease in the amounts of acid and tannin was, therefore, much larger than the increase in the quantity of total sugar. The tannin appeared to be converted into an oxidised compound. The increase in the "sweetness" of the sloe-fruit during ripening thus seems to be due to a decrease in the amounts of acids and tannin present, and to the conversion of dextrose into lævulose. W. P. S.

Microchemical and Physiological Studies on Tannin. LUIGI ERMANNO CAVAZZA (*Zeitsch. wiss. Mikroskopie*, 1909, **26**, 59—64).—A tabulated record of the microchemical reactions shown by catechol,

caffetannic acid, pyrogallol, resorcinol, phloroglucinol, vanillin, quinol, and salicylic acid with ferric chloride, ammonium metavanadate, potassium hydroxide, potassium dichromate, tellurium carbonate, gold chloride, and palladium chloride. The tannates of indium, lanthanum, iridium, yttrium, palladium, and cerium were prepared.

A comparative study of the quantity of tannin contained in the leaves and in the branches of oak, chestnut, tamarisk, fir, and other forest trees at different periods of the year showed that the amount frequently varied inversely; the tannin content of the leaves reaching its maximum in September, that of the twigs in July and December.

F. M. G. M.

Choline Content of Certain Edible Fungi. KARL POLSTORFF (*Festschrift Otto Wallach*, 1909, 579—583).—Since choline is converted, under certain conditions, by micro-organisms into neurine (compare Schmidt, Abstr., 1892, 219), the proportion of choline in three common edible fungi, namely, *Cantharellus cibarius*, *Agaricus campestris*, and *Boletus edulis*, has been estimated and found to be present to the extent of 0·01%, 0·015%, and 0·0056% respectively. It is evident, therefore, that cases of poisoning arising from eating preserved fungi are not to be attributed to the action of neurine derived from choline.

W. H. G.

Presence of Gentiopicrin in Chlora perfoliata. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1910, **150**, 114—116; *J. Pharm. Chim.*, 1910, [vii] **1**, 109—113).—Gentiopicrin has been isolated from *Chlora perfoliata*, in which it occurs to the extent of 1·5%. The product was found to be identical with the glucoside occurring in the yellow gentian. W. O. W.

Occurrence of Betaines and Choline in Drugs containing Caffeine and Theobromine. KARL POLSTORFF (*Festschrift Otto Wallach*, 1909, 569—578).—Kola beans contain from 0·25 to 0·45% of betaine in addition to caffeine and small quantities of theobromine. Coffee beans contain about 0·2% of trigonelline, whilst choline is present in cocoa beans, Indian tea, and Pasta Guarana. W. H. G.

Presence of an Alkaloid in the Seeds of Lunaria biennis. EUGÈNE HAIRS (*Bull. Acad. roy. Belg.*, 1909, 1042—1048).—The seeds yield about 1% by weight of an alkaloidal residue containing a well-defined, crystalline alkaloid and possibly a second similar substance.

The crystalline *alkaloid*, m. p. 220° (decomp.), isolated and purified in the usual way, forms slender, colourless needles, possesses a bitter taste, and dissolves readily in chloroform, but is scarcely soluble in ether or water. It is distinctly alkaline in reaction, dissolves readily in dilute acids, and gives precipitates with the usual alkaloidal reagents. Unlike the alkaloids, sinapine and cheiroline, already isolated from plants of the same natural order (*Cruciferae*), it does not contain sulphur. T. A. H.

Formation of Glucosides by means of Plants. GIACOMO L. CIAMICIAN and CIRO RAVENNA (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 594—596. Compare Abstr., 1909, ii, 604).—Not only living maize

plants, but also the pasty mass obtained by triturating them with water, are able, in presence of toluene, to decompose salicin and to transform saligenin, catechol, and, possibly, quinol and mandelonitrile into glucosides which are decomposed by emulsin. T. H. P.

Occurrence of Formic Acid in Raspberries. A. Röhrig (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 1—8).—The author has investigated the question of the occurrence of formic acid in fruits, more particularly in raspberries, the matter being of some importance seeing that this acid is employed to preserve fruits and fruit-juices and that the quantity thus added has to be estimated. He finds that fresh raspberries contain 0·000176% of formic acid, a quantity that would scarcely come into consideration when dealing with the amounts of formic acid used for preservative purposes. The method described by Wegner (Abstr., 1903, ii, 700) was employed for estimating the formic acid, it having been found to be the most trustworthy. As regards the fact that lactic acid also yields carbon monoxide when heated with sulphuric acid, the author shows that the volatile acids obtained from raspberries contain only a trace, if any, of this acid. W. P. S.

Influence of Cultivation on the Alkaloid-content of Certain Solanaciæ. J. Chevalier (*Compt. rend.*, 1910, **150**, 344—346).—The yield of alkaloids obtained from specially cultivated plants can be considerably increased by the employment of an appropriate manure. In experiments carried out on a large scale, it was found that Belladonna plants yielding 0·32—0·33% of alkaloids under ordinary conditions of cultivation, gave 0·48—0·49% when manured with phosphates and 0·40—0·61% when treated with nitrates. Under certain conditions a nitrogenous manure gave 0·75% of alkaloids for the dried leaves. Similar results were obtained in experiments on *Datura stramonium* and *Hyoscyamus*. W. O. W.

Occurrence of Anisyl Alcohol and Anisaldehyde in the Fruit of Tahiti Vanilla. Heinrich Walbaum (*Festschrift Otto Wallach*, 1909, 649—653).—Vanilla from Tahiti has not the same aroma, and is not so valuable as that from Mexico or Réunion; it is found to contain anisic acid, anisaldehyde, anisyl alcohol (*p*-methoxybenzyl alcohol), and very small quantities of substances which have not been isolated and have an intense odour. The occurrence of *p*-methoxybenzyl alcohol in nature has not been observed previously. W. H. G.

Behaviour of Plants towards Lithium Salts. Ciro Ravenna and M. Zamorami (*Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 626—630).—It is usually supposed that lithium has a highly toxic action on higher plants. Finding that the ash of tobacco leaves contains sufficient lithium to impart a marked coloration to a flame, the authors have investigated the effect of lithium sulphate on various plants. On tobacco and the potato, this salt has no toxic action, but with oats and, to a still greater extent, with beans, there is a distinct poisoning effect. T. H. P.

Accumulation of Nitrogen in Soils. A. KRAINSKY (*Centr. Bakt. Par.*, 1910, ii, **26**. 231—235).—Liquid cultures of *Azotobacter* utilise 100—200 units of sugar for 1 of nitrogen fixed. In sand cultures, owing to better aeration, the amount of carbon used is 11—30 units to 1 of nitrogen fixed. The economy of organic matter in soils is attributed to the co-operation of autotrophic organisms which in absence of light produce organic compounds by the decomposition of carbon dioxide with liberation of oxygen.

N. H. J. M.

Use of Boron as a Catalytic Manure. H. AGULHON (*Compt. rend*, 1910, **150**, 288—291. Compare this vol., ii, 241).—The addition of boric acid to a nutrient sterile medium in which wheat was grown has been found to be distinctly beneficial to the plants, unless added in amounts greater than 0·01 gram per 1000 grams of medium, when germination is prevented and the plants become etiolated. Similar results were obtained in experiments carried out under natural conditions in earth. The increased yield (calculated on the dried plant) amounted to 50% with maize, 21% with rape-seed, and 32% in the case of turnips, when a dose of 0·5 gram of boric acid per sq. metre was employed. No distinct increase occurred in the case of peas or oats. Estimation of boron in the ash showed that plants grown under these conditions contained only the normal proportion of this element. W. O. W.

Manuring with Carbon Dioxide. EILHARD A. MITSCHERLICH (*Landw. Jahrb.*, 1910, **39**, 157—166).—Two series of pot experiments are described, in which oats were grown in three different soils (sandy soil, loam, and peat soil) without manure, with complete manure, and with manures in which phosphoric acid, nitrogen, and potassium respectively were wanting. The one series was watered with tap-water, the other with water saturated with carbon dioxide.

The results showed that no increased yield was obtained by increasing the amount of carbon dioxide in the soil. A small amount of carbon dioxide rapidly increases the solubility of sparingly-soluble plant nutrients, and it would seem that under natural conditions the soil almost always contains sufficient carbon dioxide, either given off by roots or produced by the oxidation of organic matter. Application of substances for the production of carbon dioxide in the soil is therefore unnecessary. N. H. J. M.

Actions of Zinc in Pot Experiments. Contribution to the Ammonia Question. II. PAUL EHRENBERG (*Landw. Versuchs-Stat.*, 1910, **72**, 15—142. Compare Abstr., 1908, ii, 1068).—It is shown that the employment of zinc may obscure the results of pot experiments by acting sometimes favourably and sometimes unfavourably. Soils having unfavourable physical properties may be improved by the presence of zinc, especially when manured with sodium nitrate. As regards the effect of zinc on manures, it is shown that when ammonium salts are employed, the zinc may liberate a portion of the ammonia, which will act injuriously on the roots of the plants. Under sterilised

conditions, the injury will be much greater, owing to the absence of nitrification. Other possible modes of action are discussed, such as the stimulating action of zinc on plants, the poisonous effects of zinc dissolved by acid soils, etc., and the conclusion is drawn that the use of zinc should be avoided in vegetation experiments, in drainage experiments, and for collecting rain-water when the amounts and condition of the nitrogen are to be determined. N. H. J. M.

Analytical Chemistry.

Micro-chemistry with Special Reference to Behrens' Work. FRIEDRICH EMICH (*Ber.*, 1910, 43, 10—45).—A general review of the methods adopted in studying the properties of chemical substances and in their detection and estimation. J. J. S.

Automatic Gas Analysis Apparatus. KARL HOHMANN (*Festschrift Otto Wallach*, 1909, 478—495).—A somewhat complicated apparatus is described, in which one or more gas measuring tubes are combined with the ordinary Orsat pipettes, and in which the various operations involved in the exposure of the gas mixture to the absorbing reagents are effected automatically. The apparatus is designed in such a way that it can be used either with water or with mercury, H. M. D.

Gas-volumetric Estimation of Hydrogen by Catalytic Absorption. CARL PAAL and WILHELM HARTMANN (*Ber.*, 1910, 43, 243—258).—Colloidal palladium, prepared by the method of Paal-Amberger (Abstr., 1904, ii, 180; 1905, ii, 397), will absorb 300—400 times its volume of hydrogen. If the palladium-sol also contains a reducible substance, the latter is reduced by the hydrogen, and the palladium may be used to absorb further quantities of hydrogen. The authors show that this reaction may be used for the estimation of hydrogen in gaseous mixtures. The reducible substance used is sodium picrate, 2 : 4 : 6-triaminophenol being formed. The palladium-sol is contained in a modified form of Hempel pipette, and the hydrogen absorbed in the usual way. The time of absorption varies from ten to one hundred and twenty minutes, according to the mixture to be analysed. The method was tested on mixtures of hydrogen with: (1) oxygen, (2) nitrogen, (3) air, (4) carbon monoxide, (5) carbon monoxide and nitrogen, (6) carbon monoxide and air, (7) unsaturated gaseous hydrocarbons, (8) ethane, (9) ethane and nitrogen, (10) ethane and air, (11) ethane and carbon monoxide. It was also tested on coal gas. In each case the absorbable constituents other than hydrogen were absorbed by the usual reagents before absorbing the hydrogen.

It was found that when oxy-hydrogen gas was treated with the palladium-picrate-sol, it was catalysed to water, the picrate not being reduced. T. S. P.

New Reagent for Hydrogen Peroxide. K. W. CHARITSCHKOFF (*Chem. Zeit.*, 1910, **34**, 50).—A strip of filter-paper is drenched in a solution of cobalt naphthenate in benzene and then dried. The rose-coloured paper turns at once an olive-green when moistened with even very weak solutions of hydrogen peroxide.

By suddenly directing a flame on a piece of ice, traces of hydrogen peroxide will be formed, and may be detected in the liquid.

L. DE K.

The Effect of Continued Grinding on Water of Crystallisation. IRVING B. BLEEKER (*Chem. News*, 1910, **101**, 30).—On continued grinding for two hours in an ordinary Wedgwood mortar, magnesium sulphate lost 2·55%, disodium hydrogen phosphate 1·85%, and aluminium potassium sulphate 0·49%, of water of crystallisation. In the case of barium chloride, however, the salt became moist and sticky, and the amount of water was increased by 2·11%. Magnesium sulphate also became moist at first, but soon changed again to a dry and powdery condition. L. DE K.

Estimation of Chlorates in the Presence of Nitrates and Chlorides. TARAK NATH DAS (*Chem. News*, 1910, **101**, 38—39).—The solution is heated in a specially constructed flask with excess of sodium hydroxide and a definite amount of standardised stannous chloride in a current of hydrogen. The exit tube dips into a beaker containing standard iodine solution made alkaline with sodium hydrogen carbonate. When the liquid boils and the reduction is complete, the flask is cooled suddenly, thus causing the iodine to enter the flask. The solutions of the flask and beaker, together with the washings of the whole apparatus, are collected, and the excess of iodine is estimated as usual.

The iodine used in the reaction represents the excess of stannous chloride, and the stannous chloride oxidised represents the chlorate.

L. DE K.

Apparatus for the Estimation of Sulphur in Iron and Steel. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1910, **23**, 250).—An improvement on the apparatus described previously (Abstr., 1909, ii, 933). The Kipp apparatus is dispensed with, and no water need circulate through the cooler. The recoil valve introduced in the little tube inside the absorption vessel prevents all regurgitation of the liquid, and the apparatus, therefore, does not want constant attention even when there is no carbon dioxide pressure.

The flask is filled with the required amount of hydrochloric acid, D 1·52, and the absorption vessel filled with cadmium solution. The weighed sample of iron or steel is now dropped into the acid, and the cooling arrangement is then instantly put on and sealed with water. The ground joint of the cooler has at the top and the bottom a small circular opening; in the ground joint of the neck of the flask there is a small rabbet. By means of a washbottle, a cold 5% solution of sodium hydrogen carbonate is introduced through the upper hole of the cooler, and the flask is then at once heated with a small flame

until the material has completely dissolved. By turning the cooler on to the rabbet in the neck of the flask, the soda solution runs into the flask, and the carbon dioxide evolved forces any remaining hydrogen sulphide into the cadmium solution. If it should be necessary to use hydrochloric acid, D 1·19, a special washing arrangement (see the author's previous paper) must be used. L. DE K.

Estimation of Total Sulphur in Urine. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1910, **7**, 101—102).—A criticism of Ritson's paper (Abstr., 1909, ii, 827).

Desulphitation of Wine by means of Hexamethylenetetramine. ROUILLARD and GOUJON (*Ann. Falsif.*, 1910, **3**, 14—16).—Attention is drawn to the fact that hexamethylenetetramine is being used to remove excess of sulphurous acid from wines; in an acid solution, such as wine, hexamethylenetetramine undergoes decomposition with the production of formaldehyde, which combines with the sulphurous acid. The portion of the latter acid thus combined is not readily liberated on boiling the wine with the addition of phosphoric acid, and, consequently, the ordinary methods of estimating sulphurous acid in wine yield too low results should the wine have been treated with hexamethylenetetramine. The aldehyde-sulphurous acid compound formed is, however, not absolutely stable, and by acidifying such a wine with sulphuric acid and distilling, it is possible to detect formaldehyde in the distillate by means of the usual magenta-sulphurous acid reagent. White wines may be tested directly with this reagent, and the test may also be applied to red wines, without distillation, if the colouring matters is first removed by treatment with animal charcoal; in either case the wine must be acidified with sulphuric acid before the test is applied. Experiments made by the authors show that treatment with hexamethylenetetramine will apparently "remove" 75% of the sulphurous acid from a wine containing 400 milligrams of sulphurous acid per litre. W. P. S.

Volumetric Estimation of Sulphuric Acid by the Barium Chromate Method. M. HOLLIGER (*Zeitsch. anal. Chem.*, 1910, **49**, 84—93).—A slight modification of Andrews' method. The neutralised sulphate solution is heated to boiling, and precipitated by adding barium chromate emulsion, cleared just before use, with a sufficiency of hydrochloric acid. After adding a few drops of ferric chloride, the undecomposed barium chromate is precipitated by ammonia in slight excess. The filtrate and washings are then mixed with 20 c.c. of hydrochloric acid, and diluted to 400 c.c. The soluble chromate formed by the action of the sulphate on the barium chromate, which, therefore, represents the sulphuric acid, is then estimated iodometrically as usual. L. DE K.

The Heat of Chemical Reactions as a Basis for a New Analytical Method. HENRY HOWARD (*J. Soc. Chem. Ind.*, 1910, **29**, 3—4).—*Assay of fuming sulphuric acid.*—One hundred grams of the sample are weighed in a Dewar vacuum tube, 100 × 45 mm., and the

temperature (a) is noted. One hundred grams of exactly 92% sulphuric acid (temp. b) are added with stirring, and the end temperature (c) is noted. The heat of the reaction is represented by $c-(a+b)/2$, and reference is then made to a table showing the percentage of free sulphur trioxide (from 21—26%).

Assay of ordinary (96%—99%) *sulphuric acid.*—One hundred grams are weighed in the Dewar tube, and the temperature (a) is noted. One hundred grams of fuming acid (24—25% of free sulphur trioxide) (temp. b) are added, and the end temperature (c) is noted. The heat of the reaction is represented by $c-(a+b)/2$, and reference is then made to a table showing the percentage of hydrogen sulphate (from 96·6—99%).

The principle of the method may, of course, be applied in a large number of other cases, for instance, an alkali might be estimated by noting the rise in temperature on adding acid, etc. L. DE K.

Gas-volumetric Analysis with the "Decomposition Flask," and the Estimation of Nitrogen in Smokeless Powders. ERNST BERL and A. W. JURRISSEN (*Zeitsch. angew. Chem.*, 1910, **23**, 241—248).—The apparatus consists essentially of a strong, round-bottomed flask of 250—300 c.c. capacity. By means of a ground joint, a glass hood is attached, which carries at one side a dropping funnel, with a glass stopcock, and at the other side a capillary tube closed with a three-way stopcock. By turning the latter in the proper positions, communication may be established with a water air-pump, or with the Lunge nitrometer.

The analysis is carried out by treating the substance with sulphuric acid and a little mercury in a vacuum; sometimes a preliminary oxidation with chromic acid is required. The impure nitric oxide liberated, which must undergo further tests, is expelled from the flask by means of a saturated solution of sodium sulphate, and transferred to the Lunge burette. L. DE K.

Distilling Apparatus for Nitrogen Estimations by Kjeldahl's Method. WOLFGANG HEUBNER and GEORG WIEGNER (*J. Landw.*, 1910, **57**, 385—390).—A new form of bulb for attaching to the distilling flask is described with sketch. The bulb is stated to be very efficacious in preventing alkali from being carried over without prolonging the distillation. When zinc is employed, a similar bulb partly filled with glass beads is recommended. N. H. J. M.

[Modification of] Ronchèse's Method of Estimating Ammonia. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, **29**, 6—7).—The author has slightly modified Ronchèse's formaldehyde method so as to render it more generally applicable.

A $N/10$-solution is made of ammonium sulphate; a $N/5$ one in the case of other mineral ammonium salts; 10 c.c. of the liquid are then made exactly neutral to methyl-orange (methyl-red is still better), and 20 c.c. of 10% formaldehyde, neutralised immediately before use, are added. The liberated acid, which represents the ammonia, is then titrated with $N/20$-barium hydroxide, using phenolphthalein as

indicator. If the water used is quite free from carbon dioxide, the end reaction will be very sharp.

Organic salts of ammonia, provided their reaction is neutral, may also be estimated by this process. Hexamethylenetetramine may be converted into ammonium sulphate by heating with sulphuric acid, and then be treated as directed. L. DE K.

Iodometric Estimation of Phosphoric Acid. PAUL ARTMANN [and R. BRANDIS] (*Zeitsch. anal. Chem.*, 1910, **49**, 1—25).—The process is based on the determination of the ammonia contained in ammonium phosphomolybdate. One gram of the phosphate is dissolved in nitric acid with addition of a little hydrochloric acid; the solution is freed from sulphates by means of barium nitrate, and finally made up to 250 c.c.; 25 c.c. are then taken for analysis. The yellow precipitate obtained in the ordinary way is washed, by decantation, with water, and then dissolved in 4—5 c.c. of $2N$-sodium hydroxide; the filter is moistened with a little $N/2$-alkali, and then washed with 40—50 c.c. of water. To the solution are then added 20 c.c. of hypobromite solution (7·5 grams of bromine per litre), the strength of which has been carefully ascertained by titration. The liquid is now saturated with sodium hydrogen phosphate (8—10 grams), and 1·5 grams of potassium iodide are added; 15 c.c. of $4N$-sulphuric acid are now added, and the iodine liberated is then titrated as usual with $N/10$-thiosulphate.

The percentage of phosphoric acid (x) is calculated from the formula $x = a(b - c)/0{\cdot}016088d$, in which a = grams of iodine per 1 c.c. of thiosulphate, b = c.c. of thiosulphate used for 20 c.c. of hypobromite, c = c.c. of thiosulphate used in the final titration, and d = quantity (1 gram) weighed out for analysis.

Further experiments as to the suitability of the process for technical purposes are in progress. L. DE K.

Estimation of Arsenic in Copper. E. AZZARELLO (*Gazzetta*, 1909, **39**, ii, 450—453).—The author has modified the apparatus and method devised by Hollard and Bertiaux (Abstr., 1900, ii, 438) for estimating small quantities of arsenic so as to render the estimation more rapid and trustworthy. T. H. P.

Detection of Minute Quantities of Boron in the Organism and in Complex Mixtures. GABRIEL BERTRAND and H. AGULHON (*Ann. Chim. anal.*, 1910, **15**, 45—53 *).—The ash obtained is distilled with a little sulphuric acid and methyl alcohol, and the distillate is received in a platinum crucible containing a few drops of N-sodium hydroxide. The distillation is repeated after adding a little more methyl alcohol, and the mixed distillate is then evaporated to dryness.

The Turmeric Test.—The residue is dissolved in 1 c.c. of water, and acidified with hydrochloric acid. A strip of delicate turmeric paper is introduced in such a manner that only a small part of it dips into the liquid, and the other part is bent over the side of the crucible, which is then covered with a watch-glass. After a few minutes, or a few hours, according to the amount of boric acid present, the extreme

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 90—99.

end of the paper turns orange-red, and then bluish-violet on moistening with ammonia; this way is preferable to the drying at a higher temperature.

The Flame Test.—The alkaline residue is mixed with a pinch of finely-powdered calcium fluoride and a drop of sulphuric acid. A platinum wire is dipped in, and introduced in the extreme end of a pure hydrogen flame; the boron fluoride will then cause a green coloration, which may be examined spectroscopically. L. DE K.

Use of Lead Peroxide in Organic Combustions. HUGO WEIL (*Ber.*, 1910, **43**, 149).—Commercial lead peroxide always evolves carbon dioxide when heated. Samples after warming with nitric acid, or heating at 150° with syrupy phosphoric acid, still invariably give carbon dioxide when heated at 280° in a combustion tube. Material freed in this manner may be used for six or eight combustions with satisfactory results; it then absorbs carbon dioxide, and low results are obtained in the analysis. When more strongly heated, the carbon dioxide is again eliminated. The use of lead peroxide is therefore to be avoided. E. F. A.

Estimation of Carbon, Hydrogen, and Nitrogen in Highly Combustible Liquids. ERNST BERL (*Zeitsch. angew. Chem.*, 1910, **23**, 249).—Instead of weighing the liquid intended for organic combustion in small glass bulbs, the requisite quantity is dropped from a weighing pipette on to copper oxide contained in little goblets made from fine copper wire gauze. Before use these are first heated in a copper crucible and cooled in a desiccator. L. DE K.

A Simple Burette for the Estimation of Carbon Dioxide. H. H. STEPHENSON (*Chem. News*, 1910, **101**, 61).—The burette resembles a Bunte burette fitted with a three-way stopcock at each end. One tube from the lower stopcock (*B*) is connected by a rubber tube to a bottle (*C*) containing water, and the other tube to a bottle (*D*) containing aqueous sodium hydroxide, D 1·28. When required for use, (*C*) is first raised until the burette is filled. The gas, after running for a moment through the exit way of the upper stopcock (*A*), is connected with the burette, and 100 c.c. of the gas measured in the usual way. (*A*) being closed, (*C*) is lowered until the water just appears in the burette above the stopcock (*B*). The cock is turned to connect with (*D*), and the absorption of the carbon dioxide accelerated by shaking the burette and lowering the bottle (*D*). The volume of the gas is then again read off with the usual precautions. L. DE K.

Assay of Calcium Carbide, Sodium Amalgam, and Zinc Dust with the "Decomposition Flask." ERNST BERL and A. W. JURRISSEN (*Zeitsch angew. Chem.*, 1910, **23**, 248—249).—These substances may be conveniently tested by means of the authors' decomposition flask (this vol., ii, 240). *Calcium carbide* is decomposed in the evacuated flask with water saturated with acetylene, and by filling the glass with the same liquid, all the gas evolved is transferred to the measuring burette, the water-seal of which is also saturated with acetylene.

Sodium amalgam is decomposed with acidified water, and the hydrogen expelled from the flask by means of brine. Before measuring, any carbon dioxide is absorbed with potassium hydroxide.

Zinc or *zinc dust* is dissolved in hydrochloric acid with a drop of platinum chloride to accelerate the action, but copper sulphate should not be used for that purpose. Before dissolving the zinc, the air from the flask must be swept out completely by a current of carbon dioxide. L. DE K.

Quantitative Separation of Calcium and Magnesium in the Presence of Phosphates and Small Amounts of Iron, Devised especially for the Analysis of Foods, Urine, and Fæces. FRANCIS H. McCRUDDEN (*J. Biol. Chem.*, 1910, 7, 83—100, 201).—Two drops of alizarin solution are added to the solution, then ammonia until just alkaline, and then hydrochloric acid until just acid; 10 c.c. of *N*/2-hydrochloric acid and 10 c.c. of 2·5% oxalic acid are then added, and the mixture is boiled; a small amount of ammonium oxalate is added gradually to the boiling solution, which is then allowed to cool; when cold, 8 c.c. of 20% sodium acetate solution are added slowly and with constant stirring. It is then left for four to eighteen hours, filtered, and the precipitate is washed free from chlorides with 1% ammonium oxalate solution. The precipitate is then incinerated with the filter paper and weighed. The filtrate, which contains the magnesium, is evaporated nearly to dryness with nitric acid; 10 c.c. of hydrochloric acid are added, and again evaporated nearly to dryness, diluted, nearly neutralised with ammonia, and cooled; then disodium hydrogen phosphate and ammonia are added, and the magnesium weighed as pyrophosphate in the usual way with certain precautions, which are described in full. If iron is present, sodium citrate solution is added before the magnesium is precipitated. W. D. H.

Influence of Manganese on the Estimation of Magnesium in Soils. P. DE SORNAY (*Bull. Assoc. Chim. Sucr. Dist.*, 1910, 27, 671—675). —Precipitation with ammonium hydroxide fails to remove the whole of the manganese present, and on adding sodium phosphate, a precipitate, consisting of ammonium magnesium phosphate and ammonium manganous phosphate, with a trace of manganous hydroxide, is obtained. Attempts to eliminate the whole of the manganese before precipitating the magnesium were unsuccessful, owing, it is supposed, to the presence of ammonium salts. Bromine water failed to oxidise the manganese completely; and when ammonium sulphide is employed, most of the magnesium remains in the precipitate.

The method adopted was to ignite the sodium phosphate precipitate and determine the manganese present by Leclerc's method. In one soil it was found that the precipitated phosphates contained more than 50% of manganese. N. H. J. M.

New Volumetric Methods for Titrating Zinc or Lead. ERWIN RUPP (*Chem. Zeit.*, 1910, 34, 121).—*Zinc.*—10—20 c.c. of an approximately *N*/2-solution of pure potassium cyanide, which has been checked

with $N/2$-hydrochloric acid, are placed in an Erlenmeyer flask; a little water and 0·3—0·5 gram of ammonium chloride are added, and the neutralised zinc solution is then added, while rotating the bottle, until a permanent cloud is produced. One c.c. of $N/2$-cyanide = 0·008171 gram of zinc. If pure cyanide is not available, the cyanide may be checked with a standard zinc sulphate solution neutral to methyl-orange in presence of ammonium chloride.

Lead.—To 20—25 c.c. of pure $N/2$-cyanide, checked with $N/2$-hydrochloric acid and methyl-orange, is added a definite volume of lead nitrate solution neutral to methyl-orange; the whole is made up to 100 c.c., and in 50—70 c.c. of the filtrate the excess of cyanide is estimated with $N/2$-hydrochloric acid. The difference between the titrations represents the lead; 1 c.c. of $N/2$-acid = 0·05178 gram of lead. L. DE K.

Estimation of Cinnabar and Sulphur Auratum in Rubber Wares. FRITZ FRANK and KARL BIRKNER (*Chem. Zeit.*, 1910, **34**, 49—50. Compare Abstr., 1909, ii, 833).—0·5 Gram of the cut-up sample is placed in a 100 c.c. round-bottomed flask, and 10 grams of ammonium persulphate and 10 c.c. of fuming nitric acid (D 1·5) are added. The action starts in the cold, and when, after a few minutes, it is practically over, it must be completed by heating moderately on a sand-bath for fifteen to twenty minutes. Should the oxidation be still incomplete, another 3 grams of persulphate should be added little by little. The mass, which on cooling forms a solid cake, is then dissolved in hot water, if necessary, after addition of about 10 c.c. of hydrochloric acid.

The solution, which contains all the antimony and mercury present, and also the joint sulphur as sulphuric acid, is then analysed for these substances as usual. If no great accuracy is required, it is sufficient to weigh jointly the sulphides of mercury and antimony freed from excess of sulphur; extraction with yellow ammonium sulphide will leave the mercury sulphide undissolved. L. DE K.

Reaction of Titanium. HENRY J. H. FENTON (*Ber.*, 1910, **43**, 267—268).—Piccard (this vol., i, 67) has suggested that the colour obtained with dihydroxymaleic acid and compounds of quadrivalent titanium is due to tervalent titanium formed by the reducing action of the dihydroxymaleic acid. The author had previously suggested the reaction as a very delicate test for quadrivalent titanium (Trans, 1908, **93**, 1064). Further experiments have shown that tervalent titanium gives a different coloration from quadrivalent titanium. In moderately dilute solutions the latter gives a brilliant orange colour, whereas the former gives a dull yellowish-brown, which is only changed to orange on oxidation by atmospheric oxygen. T. S. P.

Microchemical Detection of Tannins. LUIGI E. CAVAZZA (*Zeitsch. wiss. Mikroscopie*, 1909, **26**, 59—64).—See this vol., ii, 233.

General and Physical Chemistry.

Refraction of Gases; its Application to Analysis. LUDWIG STUCKERT (*Zeitsch. Elektrochem.*, 1910, **16**, 37—75).—Two instruments for measuring the refractive index of a gas are described, both of which are made by Leisz of Jena. In the first the deflexion of a ray of light on passing through a prism filled with the gas is measured on a scale which is observed through a microscope. Since for analytical purposes it is convenient to measure the refractive index of the gas relatively to some other standard gas, the prism is enclosed in a box with parallel glass ends, which is filled with the standard gas. By means of this instrument the addition of 0·2% of carbon dioxide or methane to air can just be detected. Since the detection of quantities of methane as small as 0·02% in air is of importance in mines, a more sensitive instrument has been constructed. In it a parallel beam of light falls on two slits in a brass plate; the light passing through these slits gives a set of dark and light bands due to interference. In the lower half of the beam of parallel light two brass tubes are placed, one in front of each slit; the tubes contain the gas under examination and the standard gas respectively. Owing to the different retardation of the light in the two gases, the interference bands are displaced. This difference of retardation is compensated by means of a glass plate placed in the path of one of the beams; the thickness of glass through which the light has to pass is varied by rotating the plate, and the angle of rotation required to bring the two sets of interference bands into coincidence is used as a measure of the refractive power of the gas. By means of this instrument, 0·01% of methane can be detected in air.

The application of these instruments to analysis requires an accurate knowledge of the refractive indices of the gases in question. The author has determined these for a number of gases, using a Jamin interferometer, and paying especial attention to the purity of the gases used. In most cases, after a thorough chemical purification, the gases are liquefied and submitted to fractional distillation. From the observations the absolute refractive index of the gas at 0° and 1 atmosphere pressure is calculated. The following are the results:

Wave-length =	$0·4359\mu$	$0·5461\mu$	$0·6708\mu$
Carbon dioxide	1·0004589	1·0004511	1·0004466
Sulphur dioxide	1·0006963	1·0006820	1·0006606
Cyanogen	1·0008708	$\left\{\begin{array}{l}1·0008481\\1·0008595\end{array}\right\}$	1·00084308
Ethane	1·0007824	1·0007690	1·0007629
Ethylene	1·0007428	1·0007315	1·0007168
Acetylene	1·0006190	1·0006051	1·0005977

For sulphur dioxide the results are probably rather high; the refractive index was not proportional to the pressure of the gas. For $\lambda = 0·5461\mu$, the author found by another method the value 1·0006666, which he regards as more accurate. T. E.

Optical Constants of Certain Elements. H. von Wartenberg (*Ber. Deut. physikal. Ges.*, 1910, 105—120).—The author has measured the refractive index, *n*, the coefficient of absorption *nk*, and the reflexion capacity, *R*, of various metals for yellow light of wave-length $\lambda = 579$. Voigt and Drude's method was employed, and the following results obtained:

	Mn.	Cr.	V.	Ta.	Nb.	Wo.	Pd.	Rh.	Ir.	Pt.	Si.	C.
n	2·49	2·97	3·03	2·05	1·80	2·76	1·62	1·54	2·13	2·03	3·87	2·98
nk ...	3·89	4·85	3·51	2·31	2·11	2·71	3·41	4·67	4·87	4·4	0·47	1·74
R (%).	63·5	69·7	57·5	43·8	41·3	48·6	65·0	78·3	74·6	71·3	35·7	36·7

For platinum containing 10% rhodium, 1·79, 4·20, and 71·7% were the three values obtained. For iridium, rhodium, and platinum-rhodium, data for red light ($\lambda = 660\mu\mu$) are also recorded.

H. M. D.

Dispersion and Rotation-Dispersion of Certain Naturally Active Crystals. Hermann Rose (*Jahrb. Min. Beil.-Bd.*, 1910, **29**, 53—105).—Measurements have been made of the ordinary and the rotatory-dispersive powers of crystals of sodium bromate, potassium, calcium, strontium and lead dithionates, and of cinnabar. In addition, the ordinary dispersion was determined for sodium uranyl acetate, and it was found that cæsium dithionate exhibits rotatory power similar to that of the corresponding potassium and rubidium salts. The data obtained for the dispersion of sodium chlorate and cinnabar, and for the rotation-dispersion of sodium chlorate, can be satisfactorily represented by Drude's formula. This, however, is only capable of expressing the rotation-dispersion of cinnabar in an approximate manner.

In the use of the quartz mercury lamp for the dispersion measurements, seven new mercury lines of wave-lengths 592·5, 607·5, 612·7, 623·9, 672·0, 690·7, and 707·7 $\mu\mu$ were observed. H. M. D.

Occurrence of Curved Spectral Lines in the Spark Spectrum of Bismuth. Heinrich Rausch von Traubenberg (*Physikal. Zeitsch.*, 1910, **11**, 105—106).—An investigation of the spark spectrum of bismuth has shown that the spectrum of the second order contains two lines which exhibit distinct curvature. The apparatus was so arranged that the discharge from two Leyden jars took place between bismuth electrodes in a direction parallel to the slit. The curvature of the lines is such that the light coming from the centre of the spark gap is displaced towards the region of small wave-lengths. Similarly, curved lines appear to be present in the spectra of antimony, tellurium, and zinc. An explanation of the curvature has not yet been obtained, but it is improbable that it is due to a Doppler effect. H. M. D.

Absorption Spectra of Solutions. A Possible Method for Detecting the Presence of Intermediate Compounds in Chemical Reactions. Harry C. Jones and W. W. Strong (*Amer. Chem. J.*, 1910, **43**, 224—227).—Jones and Anderson (Abstr., 1909, ii, 359) and Jones and Strong (this vol., ii, 87, 172) have found that

certain salts show different absorption bands when dissolved in different solvents. It has now been discovered by a further study of absorption spectra that it is highly probable that intermediate compounds are commonly formed in chemical reactions, or, at any rate, in those in which uranium salts are involved.

When sulphuric acid is added to a solution of uranyl nitrate containing free nitric acid, the spectrum of the solution is intermediate between those of the nitrate and the sulphate. Certain of the bands of the nitrate spectrum are shifted to new positions, the amount of the shift depending on the quantity of sulphuric acid added. As the amount of sulphuric acid is increased, these bands continue to shift, until they finally occupy the position of the bands of a solution of the sulphate containing sulphuric acid. On adding hydrochloric or hydrobromic acid to a solution of uranyl nitrate containing free nitric acid, even more striking results are obtained. If nitric acid is added gradually to a solution of uranous acetate containing free acetic acid, the uranous bands gradually disappear as the uranous salt becomes changed to the uranyl salt, and, simultaneously, two pairs of the uranyl acetate bands shift their positions and finally unite into single nitrate bands. These changes indicate the possibility of the formation of a series of more or less unstable intermediate products, and it is therefore suggested that the absorption spectra may serve as a means of detecting the presence of intermediate compounds in chemical reactions. E. G.

Absorption Spectra of the Cinnamic Acids. HANS STOBBE (*Ber.*, 1910, **43**, 504, 507. Compare Biilmann, Abstr., 1909, i, 155, 382; Liebermann, *ibid.*, i, 303).—The trimorphism of the two *iso*cinnamic acids and *allo*cinnamic acid has been confirmed by the identity of their ultraviolet absorption spectra in alcoholic and also in aqueous solution. The spectrum bears to that of ordinary *trans*-cinnamic acid very much the same relation as that exhibited by the *cis*- and *trans*-modifications of other aromatic ethylene derivatives.

C. S.

Optical Isomerism. II. IWAN I. OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 102—109. Compare Abstr., 1908, ii, 913).—The author discusses the mechanism of the formation of pseudo-racemic mixed crystals, and gives the results of an examination of the various forms of (1) camphoroxime, the racemic and pseudo-racemic modifications of which do not show even temporary triboluminescence, and (2) ammonium hydrogen malate, the racemic form and the pseudo-racemic mixtures of which exhibit no triboluminescence (compare Tschugaeff, Abstr., 1905, ii, 132). The conclusion is drawn that the formation of so-called pseudo-racemic mixed crystals from enantiomorphous forms of two optical antipodes or from their racemic compounds is, in reality, a process of transformation of these antipodes into a dimorphous, holohedral modification. Further, optical antipodes, which form with one another mixed crystals only in limited proportions, do not exist; optical antipodes possess, in fact, the property of giving solid solutions with racemic forms. The crystals of ammonium

hydrogen malate observed by Pasteur (*Compt. rend.*, 1856, **42**, 1259), Kenrick (Abstr., 1897, i, 506), and van't Hoff and Dawson (Abstr., 1898, i, 299) evidently consisted of mixed crystals of the optically active malate with the racemic salt.

As regards the relation between the crystalline form and structure of asymmetric substances, the conclusion is drawn that, if a substance crystallises in enantiomorphous forms, each of its optical antipodes always prefers to separate exclusively in one of these forms, or, in other words, racemic compounds do not crystallise in enantiomorphous crystals. No exception to this rule has been observed. T. H. P.

Photochemistry of Sulphuric Acid. ALFRED COEHN and HANS BECKER (*Zeitsch. physikal. Chem.*, 1910, **70**, 88—115).—An apparatus suitable for photochemical investigations such as are discussed in the paper is described and figured. The apparatus is mainly of quartz; the reaction chamber is in the interior, and is surrounded by a mercury vacuum lamp. The interior chamber can be kept at constant temperature by passing a stream of water between it and the lamp. In the majority of the experiments the reacting gases were sealed in quartz tubes, which were placed for definite intervals in the reaction chamber. The progress of the reaction was then determined by opening the tubes under iodine solution; the remaining iodine was then titrated with sodium thiosulphate, and the total acidity with barium hydroxide.

It is shown that a photochemical equilibrium exists, represented by the equation: $2SO_2 + O_2 \rightleftharpoons 2SO_3$; the equilibrium has been reached from both sides, and when the reacting substances are present in equivalent proportions, the equilibrium mixture contains about 65% of sulphur trioxide. In daylight and at room temperature the equilibrium mixture contains about 100% of sulphur trioxide. With a certain intensity of light, the average value of $K = [O_2] \times [SO_2]^2/[SO_3]^2$ is $2 \cdot 9 \times 10^{-6}$, but when the light intensity is diminished by diminishing the current through the lamp, the equilibrium point is altered, as might be anticipated for a true photochemical equilibrium. The position of the photochemical equilibrium is independent of the temperature between room temperature and 800°. The rate at which the equilibrium is reached is much less in Uviol glass tubes than in quartz tubes.

The temperature-coefficient of the reaction $2SO_2 + O_2 = 2SO_3$ between 50° and 160° is about 1·2 for a rise of temperature of 10°.

The nature of photochemical equilibria is discussed, in which connexion it is pointed out that the possibility of the existence of a photochemical equilibrium different from the ordinary equilibrium is denied by some observers.

The conditions for applying the foregoing results in the technical production of sulphuric acid are briefly discussed. G. S.

Photochemical Phenomena in Connexion with Solutions of Dyes. KURT GEBHARD (*Ber.*, 1910, **43**, 751—753).—A criticism of Weigert's paper (this vol., ii, 174) on the same subject, the author maintaining that different observers have proved that the bleaching of

a colouring matter is due to oxidation, an intermediate peroxide of the dye being formed. T. S. P.

Paper Sensitive to Ultraviolet Light. CARL SCHALL (*Chem. Zeit.*, 1910, **34**, 267).—Paper impregnated with $2N/3$-*p*-phenylenediamine nitrate is recommended.

The paper turns blue in light with wave-lengths of from 313 to 295 λ. L. DE K.

Tables of Radioactive Constants. LÉON KOLOWRAT (*Le Radium*, 1910, **7**, 1—3).—This consists of a new and revised edition of the constants of the known radioactive substances first published a year ago (*Le Radium*, 1909, **6**, 1—3). The list comprises thirty substances, and the tables include the radioactive constant λ, with the derived periods of half-change and of average life, the nature of the radiations, the range of the α-rays in air, the absorption of the β-rays in aluminium, and of the γ-rays in lead, together with a short résumé of the chief physical and chemical properties of the substance. F. S.

The Radioactivity of Dew. C. NEGRO (*Physikal. Zeitsch.*, 1910, **11**, 189—191).—Glass plates left out overnight on the surface of the ground become coated on the under side only with dew, which, measured in an Elster-Geitel apparatus, shows an activity decaying to zero with a half-period slightly greater than half an hour. This is in accord with experiments on the radioactivity of rain and snow. Meteorological factors exert no influence. F. S.

The Determination and Convenient Estimation of the Radioactivity of Mineral Springs. FERDINAND HENRICH (*Zeitsch. angew. Chem.*, 1910, **23**, 340).—The paper contains a description of a method, more or less empirical, for the determination of the amount of radium emanation in spring water. The latter is brought into a Woulfe's bottle, nearly filling it, and, by means of a rubber bellows, air is circulated through the water and a large closed vessel in communication with it containing an Elster-Geitel electroscope. The natural leak is first determined, using distilled water, then the leak with the spring water, and finally the leak due to the active deposit alone, after the air in the electroscope vessel is displaced with fresh air. Readings are taken in each case of the fall of potential "after some time" from starting the circulation for a period of sixty minutes. Corrections are introduced for the proportion of the total air contained in the bellows and Woulfe's bottle, not in the electroscope vessel, and for the solubility of the emanation in water, the solubility being reckoned as 0·23. The total amount of emanation per litre of water is so obtained in terms of volts per hour discharge of the electroscope, the discharge in the first and third readings being subtracted from the total discharge observed in the second of the three determinations. The result is readily converted into absolute units by multiplying the volts per hour by the capacity of the electroscope in absolute units and dividing by 300×3600. This gives the leak in absolute measure

(electrostatic units per second), and this divided by 1000 gives the result in the so-called Mache units. An actual example is worked out. F. S.

Relation between the Radioactivity and Richness in Solids of the Thermal Waters of Plombières. ANDRÉ BROCHET (*Compt. rend.*, 1910, **150**, 423—425).—The radium emanation and the dissolved solids in the hot Plombières waters both come from the depths, and are diluted by cold surface waters containing little solids, so that proportionality might be expected to exist between emanation and solids. Instead, the ratio of emanation to solids increases regularly and markedly as the latter diminishes and the temperature of the water decreases. This is ascribed to the escape of emanation from the water being the greater the higher the temperature. This explains why the Bizot spring, consisting of a small quantity of deep water with much cold water, is still highly radioactive. Systematic study of temperature, dissolved solids, and the radioactivity of thermal waters should give interesting conclusions. F. S.

A Method for the Determination of the Constants of Radium-*A* Ions. JAKÓB SALPETER (*Bull. Acad. Sci. Cracow*, 1910, 23—32).—The radium-*A* atoms produced in an atmosphere containing the radium emanation are considered as ions carrying the atomic charge of positive electricity, and possessing, like the ions in a gas, definite mobility, coefficient of diffusion, and coefficient of re-combination. The mathematical expressions giving the relation between these quantities and the distribution of the deposit of radium-*A* on the anode and cathode respectively in an electric field are worked out theoretically for the case of a parallel plate condenser, with plates of infinite area, for a uniform distribution of radium emanation between the plates. The distribution of the active deposit when the concentration of the emanation, the distance between the plates, and the electric field are varied can be used to determine the constants of the radium-*A* ions. The effect of the further disintegration of the radium-*A* is neglected. The expressions deduced are complicated, and cannot be well dealt with in an abstract. F. S.

Radio chroism of Organic Substances to α-, β-, and γ-Rays of Radium and to *X*-Rays. GUILLEMINOT (*Compt. rend.*, 1910, **150**, 332—335).—A method is described for measuring the absorption of radium rays in absorbing filters by adjusting the fluorescence caused by the rays on a barium platinocyanide screen against the fluorescence produced on an adjacent part of the screen by a constant source of *X*-rays, the distance of which from the screen is varied. A table of results is given for aluminium and paraffin. The conclusion is drawn that the latter, which resembles organic tissues, possesses, relatively to aluminium, a remarkably high absorbing power for the α- and β-rays of radium. F. S.

Measurement of the Absorption of Cathode-rays in Gases by means of Secondary Rays. H. BAERWALD (*Physikal. Zeitsch.*, 1910, 11, 145—158; *Ber. Deut. physikal. Ges*, 1910, 12, 159—171).—The coefficient of absorption of cathode-rays in air, hydrogen, nitrogen,

oxygen, nitric oxide, carbon monoxide and dioxide, and sulphur dioxide, has been determined by means of the secondary rays they produce in air at atmospheric pressure. The cathode-rays, emerging from the window of a Lenard tube, traverse a space filled with the gas under examination. Into this space project two similar tubes filled with air at atmospheric pressure, each tube being provided with a central insulated electrode connected with an electrometer and bearing at its lower end a window on which the cathode rays fall, producing secondary rays inside the tubes. The windows of the two similar tubes are at different known distances from the window of the Lenard tube, so that the absorption coefficient of the rays in the gas under examination can be calculated from the ratio of the ionisation current in the two tubes. The results bear out closely the earlier ones of Becker (*Ann. Physik*, 1905, [iv], **17**, 381), the value of the absorption coefficient divided by the density being sensibly constant for all gases except hydrogen, for which the value is about five-thirds the normal. The value of the found dielectric constant for hydrogen is also greater than that calculated from the refractive index. The results bring out a connexion between the absorption of cathode-rays and the dispersion of light rays by gases. F. S.

Homogeneous Corpuscular Radiation. CHARLES A. SADLER (*Phil. Mag.*, 1910, [vi], **19**, 337—356. Compare Barkla and Sadler, Abstr., 1909, ii, 457; Barkla, this vol., ii, 8).—When a homogeneous beam of secondary Röntgen radiation from a given metal (secondary radiator) is allowed to fall on a metal of lower atomic weight (tertiary radiator), the latter is found to emit an easily absorbable radiation consisting of negatively charged particles. The author has investigated in what manner the emission of this corpuscular radiation depends on the exciting radiation.

The experimental results indicate that the corpuscular radiation exerted by secondary beams of widely different penetrating power is in every case absorbed according to an exponential formula. The absorbability of the corpuscular radiation from a tertiary radiator is entirely dependent on the penetrating power of the exciting secondary beam and not at all on the nature of the tertiary radiator. The absorption coefficient is a linear function of the atomic weight of the metal which acts as the source of the exciting beam. From the data relating to the dependence of the quantity of corpuscular radiation emitted by a given tertiary radiator on the atomic weight of the exciting secondary radiator, it is found that a large increase takes place when the atomic weight reaches a certain value, and this coincides with the point at which a large increase takes place in the amount of tertiary Röntgen radiation. It appears, therefore, that there is a connexion between the production of Röntgen radiation in a substance and the emission of corpuscular radiation by that substance. The corpuscular radiation emitted in such cases is supposed to be connected with the scattering of the rays. H. M. D.

Polonium. Mme. MARIE CURIE and ANDRÉ DEBIERNE (*Compt. rend.*, 1910, **150**, 386—389).—The treatment of some tons of residues

of uranium minerals, in order to get the polonium in as concentrated a form as possible, resulted in a product weighing 2 mg. From its α-activity, the quantity of polonium present, as calculated from the theory of radioactive change, was deduced to be of the order of 0·1 mg., or the amount present, according to theory, in 2 tons of good pitchblende. The polonium was first dissolved out of the residue by hot concentrated hydrochloric acid, and by processes not yet described was first obtained with 200 grams of matter (mainly copper, bismuth, uranium, lead, and arsenic). The activity, which was due solely to polonium, was 3500 times that of uranium. The solution in hydrochloric acid was precipitated with ammonia to remove copper, the hydroxides digested with sodium hydroxide to remove lead, and the solution treated with ammonium carbonate to remove uranium. The solution of the insoluble carbonate was treated with stannous chloride. The precipitation weighed 1 gram, and contained nearly all the polonium. Great difficulty was experienced in further purification, owing to many of the methods before successfully used failing with the purer material, but precipitation as sulphide or by stannous chloride and by electrolysis continued to be effective.

In the final product of 2 mg. a few per cent. of polonium should have been present, and the spectrum showed, in addition to many elements (gold, platinum, mercury, lead, rhodium, and iridium), lines at 4642·0 (feeble), 4170·5 (strong), 3913·6 (feeble), 3652·1 (very feeble), which with three other doubtful lines may prove to be due to polonium. The spectrum is to be re-examined when all the polonium has disintegrated, which should decide the matter. Lead, whilst not totally absent, was very feeble in the spectrum, and it is expected that the re-examination will prove whether lead is the final product of the disintegration. The substance gave no penetrating rays and no active deposit, whilst radium could be only just detected by its emanation.

A part of the substance in solution in an exhausted quartz vessel disengaged gas, and the formation of bubbles could be observed. The residue of inert gas left after absorbing the common gas was pure helium. About 1·3 cu. mm. of helium was produced in one hundred days of accumulation, the theoretical volume calculated from the number of α-particles expelled being 1·6 cu. mm. The preparation produced ozone abundantly. A quartz capsule containing the dry substance became covered with cracks, probably caused by electric discharges. F. S.

Attempted Separation of Uranium and Uranium-*X* by Electrolytic Methods and by Cathode Volatilisation. G. VON SENSEL (*Zeitsch. physikal. Chem.*, 1910, 71, 563—570).—In the electrolytic experiments, concentrated aqueous solutions of uranium oxalate, acetate and nitrate were subjected to electrolysis at potentials varying from 0·05 to 1·5 volts. The products contained excess of uranium-*X*, usually from 7—12%, and in one case as much as 45%, but a complete separation by this method was not found possible.

In the cathode volatilisation experiments, black uranium oxide was placed in the hollowed-out cathode, opposite which was a disk of copper. After prolonged discharge, the copper plate was found to

be active, so that "volatilisation" (Zerstäubung) had occurred, but uranium and uranium-X were present in equilibrium proportions (compare Greinacher, Abstr., 1908, ii, 551). G. S.

Emission of Electric Charges by the Alkali Metals. LOUIS DUNOYER (*Compt. rend.*, 1910, **150**, 335—338).—The experiment of J. J. Thomson on the emission of negative electrons from rubidium in total darkness has been repeated. An exhausted glass tube, which contained the rubidium, carried axially two platinum wires 25 mm. apart, the one connected to a battery and the other, which was surrounded by a platinum tube to serve as a guard ring, connected to an electrometer. The whole was enclosed in two concentric brass tubes, blackened internally and externally. Work was carried on in a dark room, and the lamp for reading the electrometer was carefully shielded by a box and only lit for a few seconds to take readings. A current rising from 0·8 to 60 ($\times 10^{-14}$ amp.) as the potential of the battery was increased from 50 to 110 volts was observed. A narrow pencil of light arranged not to fall on the metal or the electrodes increased the current 10,000 times. When the openings in the box by which the pencil was admitted were covered completely with half tubes of brass, an Auer light at $1\frac{1}{2}$ metres distance doubled the current. This suggested that the phenomenon might be due to light of very long wave-length diffracted through the covered openings. It is suggested that the action in total darkness is due to long radiations from substances of ordinary temperature, rather than to spontaneous explosion of the atoms analogous to radioactivity, and it is proposed to try the effect at very low temperature. F. S.

Change of the Conductivity of Solid Cuprous Iodide in the Light. GERHARDT RUDERT (*Ann. Physik*, 1910, [iv], **31**, 559—596). —For the purpose of the conductivity measurements, thin layers of cuprous iodide were prepared by exposing glass plates to the action of a disintegrating copper cathode and subjecting the copper mirrors thus obtained to the action of iodine vapour.

When the cuprous iodide is exposed to light, a gradual increase of the electrical conductivity is observed, a reversal of this effect being obtained when the source of light is removed. No special instantaneous light effect can be detected. The effectiveness of the light rays increases as the wave-length diminishes. The action of the red rays can only just be detected, and it is not until the blue region is reached that rays of any considerable activity are met with. In general, the change in conductivity is proportional to the absorption of the rays by the cuprous iodide.

For very short intervals of illumination, the effects are proportional to the light intensities; for longer time intervals, the conductivity changes increase less rapidly than the light intensities. The absolute as well as relative increase in conductivity on exposure to a standard light is found to be the greater the greater the resistance of the unexposed cuprous iodide.

In explanation of the observations, it is supposed that the light causes dissociation of the cuprous iodide, whereby iodine is liberated.

In consequence of the tendency to recombination, a condition of equilibrium is set up after lapse of a certain time interval. The iodine liberated in the photochemical dissociation process dissolves in the cuprous iodide, and imparts to this an increased metallic conductivity. H. M. D.

Electrical Conductivity of Certain Metallic Nitrides. IWAN I. SHUKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 40—41).—The electrical conductivities of certain powdered metals and powdered metallic nitrides in reciprocal ohms per cube of 1 cm. side are as follows: iron, 27·0; aluminium, 38·46; chromium, 38·46; manganese nitride, 18·18—22·62; chromium nitride, 15·40—12·72; titanium nitride, 31·05. Aluminium nitride, AlN, calcium nitride, Ca_3N_2, and magnesium nitride, Mg_3N_2, show resistances of more than 2×10^6 ohms. These nitrides hence form two classes, those of magnesium, chromium, and titanium exhibiting conductivities of the same order as those of pure metals, and those of aluminium, calcium, and magnesium having very small conductivities. The numbers given above are naturally only of a qualitative character. T. H. P.

Dielectric Constants of Solvents. PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1910, **70**, 569—619).—The dielectric constants of sixty carefully purified substances, mostly organic liquids, have been determined at a series of temperatures by Nernst's method (for $\lambda = \infty$), and the relations between these constants and other chemical and physical properties of the media are discussed in detail (compare Abstr., 1909, ii, 119, 122, 547).

The dielectric constants are as follows: Ethyl alcohol, 28 8, 25·4, 20·8 at 1·5°, 18·5°, and 49·2°; ethylene glycol, 46·7, 41·2, 35·5 at 1°, 20°, and 50·5°; benzyl alcohol, 15·8, 13·1, 10·4 at 1°, 19°, and 49°; furfuraldehyde, 46·9, 42·0, 34·9 at 1°, 19·5°, and 50°; phenylacetonitrile, 19·95, 18·23, 16·80 at 1·3°, 21·5°, and 51°; benzonitrile, 28·6, 26·2 at 1·5° and 22·4°; acetonitrile, 41·8, 38·8 at 1·5° and 20°; propionitrile, 31·3, 27·5, 24·6 at 1°, 21°, and 50°; nitrobenzene, 40 3, 35·5, 30·2 at 0°, 20·5°, and 50·5°; nitromethane, 44·8, 39·4 at 1·5° and 20°; methyl formate, 9·20, 8·23 at 1° and 20 8°; ethyl nitrate, 21·2, 19·6, 16·9 at 1·1°, 20·7°, and 50°; acetophenone, 18·6, 18·1, 15·1 at 14°, 21°, and 56°; benzophenone, 13·3, 11·3 at 21° and 63° (metastable form); 11·2 at 63°, 12·2 at 46°, 12·5 at 37°, 13·2 at 21° for stable form in liquid (supercooled) state; 3·1 at 25·5° for stable form in solid state; anisole, 4·7, 4·3, 3·9 at 4°, 23·4°, and 56°; ethylene chloride, 11·55, 10·45, 9·4 at 1°, 19·8°, and 50°; acetone, 23·3, 21·2 at 1° and 22°; chloroacetic acid, about 21 at 20° (solid); about 20 at 62° (liquid); dichloroacetic acid, 8·8 at −9° (liquid); 8·2 at 22° (liquid); 7·8 at 60·5°; trichloroacetic acid, 4·55 at 61° (liquid); cyanoacetic acid, about 33·4 at 4° (solid); ethyl dichloroacetate, 11·6, 10·3 at 2° and 22°; ethyl trichloroacetate, 8·3, 7·8, 6·7 at 2°, 20·5°, and 60°; ethyl bromopropionate, 10 0, 9·3 at 2° and 22°; ethyl cyanoacetate, 27·7 at 21°; ethyl sulphite, 17·5, 15·9, 13·7 at 1°, 19·5°, and 50·4°; ethyl ethanesulphonate, 45·5, 41·9 at 1·2° and 20°; methyl sulphate, 58·3, 54·8 at 3° and 21°; *iso*butyl ricinoleate, 4·7 at 21°; acetic anhydride, 22·4,

20·7 at 1° and 18·5°; acetyl chloride, 16·9, 15·8 at 2° and 22°; triethylamine, 3·15 at 21°; benzylamine, 5·5, 4·6, 4·3 at 1°, 20·6°, and 50°; methylaniline, 7·85, 5·93 at 1·3° and 20·8°; dimethylaniline, 4·8, 4·48, 3·9 at 2°, 20°, and 51·8°; ethylaniline, 6·3, 5·9 at 1·5° and 19·8°; ethyl bromide, 10·5, 9·4 at 1·4° and 21°; bromobenzene, 5·46, 5·21, 4·64 at 1·2°, 23·5°, and 50°; allyl chloride, 8·7, 8·2 at 1° and 20°; allyl bromide, 7·4, 7·0 at 1° and 19°; acetylene tetrabromide, 8·6, 7·0 at 2·5° and 21·5°; tetranitromethane, 2·15 at 5° (solid), 2·13 at 23·4°; acetaldoxime, 2·98 at 22·6°; nitromethane, 44·8, 39·4 at 1·5° and 20°; ethyl thiocyanate, 34·6, 29·3 at 2·5° and 21°; ethylthiocarbimide, 23·4, 19·5 at 2° and 21°; acetylacetone, 25·9, 23·4 at 1° and 18·2°; paraldehyde, 14·6, 11·6 at 20·3° and 52·5°; benzaldehyde, 19·9, 18·1 at 1·3° and 19·5°; acetal, 3·45 at 24°; ethylene oxide, 13·9 at −1°; epichlorohydrin, 25·5, 22·6 at 1·5° and 22°; α-chlorohydrin, 37·4, 31 at 3° and 19°; bromine, 4·6 at 1°; sulphur chloride, S_2Cl_2, 5·3, 4·9 at 12° and 22°; tin tetrachloride, 3·2 at 22°; phosphorus trichloride, 4·7 at 22°; phosphoryl chloride, 12·7 at 22°; thiophosphoryl chloride, $PSCl_3$, 5·8 at 21·5°; sulphuryl chloride, SO_2Cl_2, 10·0 at 21·5°. The results are in fair agreement with those of previous observers, even when determined by Drude's method, for which the wave-length is not infinitely great.

The Clausius-Mosotti expression: $(K-1)/(K+2)d$, where K represents the dielectric constant and d the density, is not constant, as the theory requires, but in some cases increases, in others diminishes, with rise of temperature.

An examination of the data indicates that all substances with high dielectric constants possess certain "dielectrophore" groups, OH, NO_2, CO (as COH, =CO and COOH), SO_2, CN, SCN, NCS, NH_2, and the halogens, all of which are negative groups. When these groups are combined among themselves, however, the dielectric constant is low, and an accumulation of them in the same molecule also lowers the dielectric constant. In order that a high dielectric constant may result, the dielectrophore groups must be combined with positive "dielectrogene" groups, of which the most important are hydrogen and alkyl groups.

As regards relationships between physical properties and composition, the relationship $R^2.\gamma_\sigma/T_\sigma$ = constant, where R^2 is the molecular refraction, γ the surface-tension, and T_σ the absolute temperature of the boiling point, is tested from the available data. It holds approximately at the boiling point for many non-associated compounds of the fatty series, the constant varying from 1·20 to 1·25; for certain non-associated aromatic compounds it is greater than 1·2, and for associated compounds less than 1·2. Further, it is shown that for non-associated solvents the quotient of the refraction r^2 and the specific cohesion is approximately constant and =0·062, and also the quotient of the heat of vaporisation, λ, by the refraction is constant and =310. These relationships do not hold for associated substances.

As regards relationships between the dielectric constants and other physical properties of solvents, the expression $\frac{K-1}{K+2}.\frac{M}{d}.\frac{\gamma_\sigma}{T_\sigma}$ = const. is

deduced, and is shown to be valid at the boiling point for a large number of substances, the magnitude of the constant being about 3·6. In this case also, associated compounds and certain other substances do not follow the rule. Further, the surface-tension, γ, at 20°, divided by the molecular weight of the substance, goes parallel with the dielectric constant for aliphatic, but not for aromatic compounds.

The following relationships: K_s/K_1d_σ = const. and $(K_\sigma - 1)/(K_\sigma + 2)\pi_1$ = const., where K_s is the internal pressure (compare Abstr., 1909, ii, 122), $K_1 = (K - 1)/(K + 2)d$, and π is the critical pressure, have also been found to hold for certain groups of substances. Finally, it is shown that the expression $M.K_1 = 0{\cdot}18T$ is approximately valid for a large number of substances; in words, this indicates that the molecular internal volume, deduced from dielectric measurements, is approximately proportional to the absolute temperature of the boiling point of the substance. G. S.

Conductivities, Dissociations, and Temperature-coefficients of Conductivity between 35° and 80° of Solutions of a Number of Salts and Organic Acids. ALPHONSO M. CLOVER and HARRY C. JONES (*Amer. Chem. J.*, 1910, **43**, 187—223).—In earlier work (Abstr., 1902, ii, 59; 1905, ii, 794; 1908, ii, 1011), the conductivity, percentage dissociation, and temperature-coefficients of various substances have been determined at temperatures between 0° and 35°. In the present investigation, the measurements have been made at temperatures between 35° and 80°. The results obtained at various dilutions are recorded for lithium chloride, sodium chloride, bromide, nitrate and sulphate, potassium chloride, bromide, nitrate, sulphate, chromate and benzoate, ammonium chloride, nitrate and sulphate, barium chloride and nitrate, magnesium nitrate and sulphate, silver nitrate, and also for oxalic, malonic, succinic, acetic, benzoic, phthalic and salicylic acids.

The results show that the temperature-coefficients of conductivity of aqueous solutions of electrolytes between 35° and 65° are greater the more complex the hydrates formed by the electrolyte, but are of the same order of magnitude for substances having approximately the same hydrating power. The temperature-coefficients for any given substance increase with the dilution, the increase being greatest for substances with the largest hydrating power. These conclusions follow directly from the assumption that the change in conductivity with change of temperature is largely due to the decreasing complexity of the hydrates formed about the ions as the temperature rises. Curves have been constructed for several compounds by plotting the molecular conductivities as ordinates and the temperatures as abscissæ. These curves are almost straight lines. The dissociation tends in general to decrease slightly as the temperature rises.

Comparatively few determinations were made at 80°, since several sources of error are liable to be introduced at this temperature.

E. G.

Conductivity and Ionisation of Salts, Acids, and Bases in Aqueous Solutions at High Temperatures. ARTHUR A. NOYES, A. C. MELCHER, HERMON C. COOPER, and G. W. EASTMAN (*Zeitsch. physikal. Chem.*, 1910, **70**, 335—377).—A more detailed account of work already published (compare Abstr., 1908, ii, 347; Kato, Abstr., 1909, ii, 538). G. S.

Hydrolysis of Ammonium Acetate and the Ionisation of Water at High Temperatures. ARTHUR A. NOYES, YOGORO KATO, and ROBERT B. SOSMAN (*J. Amer. Chem. Soc.*, 1910, **32**, 159—178).—Noyes and Coolidge (Abstr., 1904, ii, 226) have described a method of determining the electrical conductivity of aqueous solutions at temperatures up to 306°. This method has been applied by Noyes (Abstr., 1908, ii, 347) to the measurement of the conductivity of various salts, bases, and acids. A study has now been made of the hydrolysis of salts into free acid and base by measuring the change of conductivity produced on addition of an excess of the weak acid or base. From a knowledge of the degree of hydrolysis and of the ionisation of the acid and base, it is possible to deduce the degree of ionisation of the water. Measurements have been made of the hydrolysis of ammonium acetate and of the ionisation of ammonium hydroxide and acetic acid at 100°, 156°, 218°, and 306°, and also of the conductivity of ammonium chloride and sodium acetate at 18°, 25°, 100°, 156°, 218°, and 306°.

It has been found that the percentage hydrolysis of ammonium acetate in 0·01*N* solution is 0·35 at 18°, 4·8 at 100°, 18·6 at 156°, 52·7 at 218°, and 91·5 at 306°. The hydrogen-ion concentration in pure water increases extremely rapidly between 0° and 100°, but less so between 100° and 218°, and afterwards passes through a maximum (between 250° and 275°), and finally decreases. The following values ($C_H \times 10^7$) are recorded: at 0°, 0·30; at 18°, 0·68; at 25°, 0·91; at 100°, 6·9; at 156°, 14·9; at 218°, 21·5; and at 306°, 13·0.

The great increase in the amount of hydrolysis of ammonium acetate at high temperatures is in accord with the fact that the ionisation of weak acids and bases decreases rapidly with rising temperature, and that this acts in the same direction in increasing the hydrolysis of salts as does an increase in the ionisation of water. The increase in hydrolysis is also shown by sodium acetate and ammonium chloride in 0·01*N* solution, which are hydrolysed to the extent of 0·02% at 18°, 1·6% at 218°, and 3·4—4·1% at 306°.

From the ionisation constants of water, values of the internal energy increase attending the ionisation of water have been calculated. The values thus obtained for 0° and 25° agree with those for the heat of neutralisation obtained directly by Wörmann (Abstr., 1906, ii, 148).

It is suggested that the fact that the ionisation of water continues to increase up to so high a temperature as 250° or 275° is due to the highly associated nature of water at low temperatures. As the temperature rises, the proportion of H_2O molecules rapidly increases, and thus, although the number of ionised molecules may steadily decrease, the actual concentration of the ions continues to increase until a large proportion of the complex water molecules have become dissociated. E. G.

Electrode Potentials and Electrochemical Reactions. WLADIMIR KISTIAKOWSKY (*Zeitsch. physikal. Chem.*, 1910, 70, 206—211).—The differences of potential, ϵ_h, between a number of metals and the normal solutions of their salts, referred to the hydrogen electrode as standard, have been calculated from thermochemical data for the reaction $N/1$-metal + $H^{\cdot} = \frac{1}{2}H_2$ + metallic ion + Q, where Q is the heat of the reaction. The value of ϵ_h is obtained by dividing Q by 23·1. In all cases where comparison is possible, except for magnesium and aluminium, there is fair agreement between the observed and calculated values of ϵ_h. For the two metals in question, it is suggested that the value of Q is that representing the decomposition of water by the metals, as represented by the equations: $\frac{1}{2}Mg + H_2O = \frac{1}{2}Mg(OH)_2 + \frac{1}{2}H_2 + 40{\cdot}28$ kilog. cal. and $\frac{1}{3}Al + H_2O = \frac{1}{3}Al(OH)_3 + \frac{1}{2}H_2 + 30{\cdot}62$ kilog. cal. When these values of Q are divided by 23·1, the values $\epsilon_h = 1{\cdot}74$ volts and $\epsilon_h = 1{\cdot}32$ volts are obtained for magnesium and aluminium respectively. This value for magnesium is in good agreement with that observed by the author.

If the above view as to the nature of the reactions at magnesium and aluminium electrodes is correct, the respective values of ϵ_h should be independent of the metallic-ion concentration, but should depend on the $H^{\cdot}$ and OH' ion concentration of the solutions, and for magnesium this is shown to be the case. G. S.

Reduction of Zinc by Mercury and the Electromotive Force of Zinc Amalgams. J. L. CRENSHAW (*J. Physical Chem.*, 1910, 14, 158—183).—The equilibrium conditions in the system mercury, zinc sulphate, and water have been investigated. The method employed was very similar to that used by Hulett and Delury (Abstr., 1909, ii, 11) for the system mercury, cadmium sulphate, and water. Special precautions were taken to exclude all oxygen from the systems used, and all potential measurements were referred to a two-phase amalgam containing about 5% of zinc as standard, since at a given temperature the potential of all zinc amalgams containing something over 2% of zinc is constant.

A saturated zinc amalgam has D^{25} 13·34333, and contains 2·2196 grams of zinc to 100 grams of mercury. The relation between the density and composition of zinc amalgams is accurately represented by the formula D^{25} 13·5340 – 0·0859p, where p is the numbers of grams of zinc in 100 grams of mercury.

Cells made of amalgams ranging in concentration between 2 grams of zinc to 1000 grams of mercury and 1 gram of zinc to 10 million grams of mercury show *E.M.F.*'s which are in accordance with the gas laws and Nernst's equation. The *E.M.F.*'s between more concentrated amalgams are too small to agree with Nernst's equation.

Accurate measurements could not be made with amalgams more dilute than those mentioned above, since the potential fell rapidly, owing to the amalgam losing some of its zinc. This indicates that the reaction $Zn + Hg_2^{\cdot\cdot} \rightleftarrows Zn^{\cdot\cdot} + 2Hg$ is reversible, and that a definite equilibrium is reached in the system mercury, zinc sulphate, and water. T. S. P.

Electrocapillarity. GEORG MEYER (*Zeitsch physikal Chem.*, 1910, 70, 315—329).—The observations were undertaken with the object of throwing light on the theory of the capillary electrometer. As electrometer liquids, solutions of sulphuric acid, of potassium sulphate, and of zinc sulphate, saturated with mercurous sulphate, were used, and the effect of the addition to the mercury of small amounts of potassium, of sodium, and of zinc was observed. The mercury or the amalgam was allowed to flow into the electrometer liquid from a capillary tube, and the surface-tension determined from the capillary vibrations, which were registered photographically.

The alteration of the surface-tension of mercury against solutions of sulphates produced by addition of mercurous sulphate is represented satisfactorily by means of the equation $a = [100 \log.(1 - be^{-kc})]/[\log.(1 - b)]$, where c represents the normality with reference to the mercurous salt, b and k are constants, and the surface-tension corresponding with $c = 0$ is put $= 100$. The surface-tension of mercury against solutions of alkali salts is diminished by the addition of alkali metals to the mercury; up to concentrations of 0·0006%, the diminution is slight, from 0·0006% to 0·001% it is relatively great, and further addition then has only a slight effect. Experiments are also described in which the effect of the addition of mercuric and mercurous thiocyanates to a solution of potassium thiocyanate on the surface-tension between the latter solution and mercury has been investigated.

The bearing of these results, more particularly on the nature of the descending branch of the *E.M.F.* surface-tension curves, is discussed (compare Krüger, Abstr., 1903, ii, 707). G. S.

Improved Form of the Cadmium Normal Cell. ERNST COHEN and HUGO R. KRUYT (*Chem. Weekblad.*, 1910, 7, 171—175. Compare this vol., ii, 178).—A new form of cadmium standard cell suitable for transmission by post is described. A. J. W.

Application of the Theory of Electrolytic Ions to Fused Salts. I. RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1910, 70, 230—238).—A summary of the author's recent work on this subject (compare Abstr., 1907, ii, 152, 430, 438, 665, 735, 927; Abstr., 1908, ii, 156, 656, 1023). G. S.

Transfer Resistance in the Case of "Reversible" Electrolytic Metal Deposition. HENRY J. S. SAND and THOMAS P. BLACK (*Zeitsch. physikal. Chem.*, 1910, 70, 496—510. Compare Abstr., 1901, ii, 82; 1905, ii, 134; Coffetti and Foerster, Abstr., 1905, ii, 796).—If the precipitation of a metal on a cathode were completely reversible and no changes of concentration or similar effects occurred in the electrolyte, the difference of potential cathode/electrolyte would be independent of the current for all current densities. This is known not to be the case, and the present paper contains an account of investigations of the differences between the potential-difference cathode/electrolyte during the passage and in the absence of a current for certain metals in contact with solutions of their salts. The results are stated in terms of "transfer resistance" (Gore), the apparent

resistance per unit area of the electrode during the passage of a current.

Two forms of measuring apparatus are described and figured. In the second form, which was specially designed to secure uniform current density over the surface of the cathode, the latter consisted of a rapidly rotating copper sphere. Most of the experiments were made with copper in solutions of copper sulphate, but solutions of zinc sulphate and of bismuth nitrate were also used.

Transfer resistance is a very variable quantity, depending not only on the current strength, but also on the previous treatment of the cathode. It can be greatly diminished by passing a large current through the solution before the definite observations are made. It is probably due, in part at least, to impurities in the electrolyte, but there is some evidence that when the electrolyte has been "cleared" by passing a large current through it for some time, there is a definite limit for the transfer resistance for each current density.

Transfer resistance is greatly increased by the addition of colloids to the electrolytes, and is greatly diminished by rise of temperature, both in pure solutions and in those to which colloids have been added.

The potentials between zinc and copper and solutions of their respective salts are affected by stirring the electrolyte in such a way that the metals become more noble while the stirrer acts, but return to their original potential when the stirring is stopped.

Certain polarisation phenomena observed in solutions to which colloids have been added are described. G. S.

Electrically Controlled Thermostat and other Apparatus for the Accurate Determination of the Electrolytic Conductivity of Highly Conducting Solutions. JOHN GIBSON and G. E. GIBSON *Proc. Roy. Soc. Edin.*, 1910, 30, 254—264).—The heating was effected by electric lamps with long glass necks, placed in the water of the thermostat. The regulator, of spiral form, was filled with toluene and mercury in the usual way; when the temperature rose, the mercury made contact with a platinum point, and by the action of a relay the lamp was extinguished. The arrangements are fully described and figured. The temperature remained constant to within 1/1000°.

A conductivity cell specially designed to avoid polarisation and heating effects was used. For sulphuric acid, the narrow part of the apparatus between the electrodes was 6 cm. long and 1·5 mm. in diameter. The platinum electrodes were of wire, wound in the form of a hollow cone, so as to give a uniform distribution of the lines of flow.

The apparatus has been used to determine the electrical conductivity of solutions of sulphuric acid. Some of the results, in terms of the specific conductivity at 18°, are as follows: 0·36624 for 60·78% acid, 0·47357 for 54·45%, 0·60221 for 46·43%, 0·73556 for 33·50%, 0·74184 for 30·91%, 0·73001 for 26·44%. The results appear to be accurate to about three in 10,000. G. S.

The Contraction of Metals and Alloys During Cooling. FRIEDRICH WÜST (*Metallurgie*, 1909, 6, 769—792).—An apparatus is

described by means of which the contraction of a bar of metal during cooling from the freezing point is measured. Helical wires are embedded in the ends of the rod, and transmit the changes of length to pistons working in cylinders filled with water, so displacing a column of water in a graduated tube. Lever connexions are in this way avoided. The record begins when sufficient metal has frozen to form an outer shell of crystals. A cooling curve is taken simultaneously, and a method of plotting curves showing the variation of length with temperature is described. The amount of contraction is usually much less than that calculated by extrapolating the expansion formulæ obtained from measurements between 0° and 100°. The method does not give satisfactory indications of the change of volume during solidification.

Alloys consisting of conglomerates of the pure component metals contract less than their components, the eutectic alloy having the smallest contraction. If solid solutions are formed, on the other hand, the alloys show an increased contraction. An alloy containing 49·88% Bi, 32·47% Pb, and 17·38% Sn expands rapidly between 70° and 30°, the final volume being 0·3% greater than that at the freezing point. C. H. D.

A Thermometer for Melting-point Determinations. Julius Bredt (*Chem. Zeit.*, 1910, **34**, (26), 221).—Above the mercury bulb, the stem of the thermometer is widened somewhat, and on this wider portion four small grooves are cut parallel to the axis of the thermometer, in which the melting-point tubes are placed. E. J. R.

The Nitrogen Thermometer from Zinc to Palladium. Arthur L. Day, Robert B. Sosman, and Eugene T. Allen (*Amer. J. Sci.*, 1910, [iv], **29**, 93—161. Compare Abstr., 1908, ii, 1013).—In continuation of the previous experiments, the behaviour of the nitrogen thermometer has been examined up to a temperature of 1550°. In all essential particulars the gas-thermometer apparatus was similar to that already described. On account, however, of the contaminating effect of the iridium on the platinum-rhodium thermo-elements at temperatures above 1100°, the platinum-iridium bulb was replaced by one consisting of 80 parts of platinum and 20 parts of rhodium.

The melting points of the very nearly pure metals and salts which were used as fixed points in establishing the nitrogen scale are as follows: zinc, 418·2° ± 0·3°; antimony, 629·2° ± 0·5°; silver, 960·0° ± 0·7°; gold, 1062·4° ± 0·8°; copper, 1082·6° ± 0·8°; diopside, 1391·2° ± 1·5°; nickel, 1452·3° ± 2·0°; cobalt, 1489·8° ± 2·0°; palladium, 1549·2° ± 2·0°; anorthite, 1549·5° ± 2·0°. On account of the discovery of a small source of error, the values now recorded for the metals of lower melting point differ slightly from those given previously (*loc. cit.*). Incidentally, the melting points of cadmium (320·0° ± 0·3°) and aluminium (658·0° ± 0·6°) were determined. From the fact that the differences of temperature between the melting points of platinum and palladium as given by different observers are in good agreement, the authors estimate that the melting point of platinum in the nitrogen scale is 1755° ± 5°.

From a comparison of the thermo-element readings with the nitrogen scale, it is found that the whole range of temperature between 300° and 1550° cannot be represented by a single parabolic formula. Such formulæ can, however, be used between 300° and 1100° and between 1100° and 1550°. H. M. D.

Change of the Emissive Power of Metals with the Temperature in the Short-waved Portion of the Ultra-red. HEINRICH RUBENS [with E. HAGEN] (*Ber. Deut. physikal. Ges.*, 1910, 172—176).—The temperature-coefficient of the emissive power of metals and alloys is very small for rays of the visible spectrum, whilst for rays between $\lambda = 8{\cdot}85\mu$ and $26{\cdot}0\mu$ it varies with the electrical resistance, σ, according to the formula: $I = 36{\cdot}5\sqrt{\sigma/\lambda}$, and this has led the author to examine the behaviour of metals for ultra-red rays in the intermediate region.

Observations were made on platinum and platinum-rhodium between 400° and 1400°. For $\lambda = 2\mu$ the variation of the emissive power with the temperature is practically the same as in the case of a black body. For $\lambda = 4\mu$ the temperature-coefficient is considerably greater than for a black body, and for $\lambda = 6\mu$ the variation of the emissive power with the temperature is almost exactly that required by the above electro-magnetic formula.

By a modified method, experiments were also made with nickel and constantan at temperatures up to about 300°.

In the case of constantan the emissive power was found to be independent of the temperature for all the wave-lengths investigated.

On the other hand, the behaviour of nickel varies with the wave-lengths of the rays used. For $\lambda = 0{\cdot}78\mu$, 1μ, and 2μ, the temperature-coefficient is very small; with increasing wave-length it increases, and for $\lambda = 5\mu$ attains approximately the value required by the electromagnetic formula. H. M. D.

Measurement of Specific Heats. ALFRED MAGNUS (*Ann. Physik*, 1910, [iv], 31, 597—608).—The calorimetric apparatus consists of two similar vessels, each containing about 60 litres of water, the vessels being placed in close proximity to each other in a well insulated wooden box. Uniformity of the temperature of the water in each vessel is attained by mechanical stirring, and exchange of heat with the exterior by conduction through the parts of the stirring mechanism is reduced to a minimum by the use of glass rod carriers for the stirrers. The substance of which the specific heat is to be determined is heated in a vapour-jacketed or electrically heated copper tube, and special precautions are taken to avoid loss of heat by vaporisation of the surface layers of water when the hot substance is allowed to fall into one of the calorimeter vessels. The resulting change in the difference of temperature between the contents of the two vessels is measured by means of a copper-constantan thermopile of 100 elements, which is connected up with a low resistance mirror galvanometer. The alternate junctions of the pile are suitably supported in the two calorimeter vessels. The sensitiveness of the thermo-

electric arrangement is such that a diflexion of 0·1 mm. on the galvanometer scale corresponds with a change of temperature of 0·00002°.

Measurements of the specific heats have been made for various metals and halogen salts. For the atomic heats of the metals, the following numbers are recorded: lead, 18—100°, 6·409; 16—256°, 6·606; aluminium, 16—100°, 5·750; 16—304°, 6·097; 17—547°, 6·475; silver, 17—507°, 6·460; 16—614°, 6·641; copper, 15—238°, 6·048; 15—338°, 6·090. H. M. D.

Specific Heat at Low Temperatures. I. WALTHER NERNST, F. KOREF, and F. A. LINDEMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247—261).—A new form of calorimeter is described, which consists of a cylindrical block of copper weighing about 400 grams. A concentric cavity within the copper cylinder serves for the reception of the heated or cooled substance, the specific heat of which is to be determined. In order to obtain satisfactory thermal isolation, the calorimeter is placed is a thin-walled Dewar vessel, and the space between the copper and the glass is filled with Wood's metal. Changes in temperature are measured by means of a battery of ten iron-constantan thermo-elements, the alternate junctions of which are surrounded by small glass tubes, which are let into the metal of the calorimeter. Thermal contact between the junctions and the calorimeter is ensured by filling the cavities in the metal and the insides of the glass tubes with Wood's metal. The opposite series of junctions is similarly encased in a block of copper, which is placed in the upper portion of the calorimeter chamber. The electromotive force, which results from a change in temperature of the calorimeter, is measured by means of a milli-voltmeter, the sensitiveness of which is such that an alteration of 1° corresponds with 20 scale divisions. This scale can be read accurately to 1/10 of a division. The apparatus must be calibrated by experiments with substances of known specific heat.

Measurements of the specific heats of various substances, including metals, salts, acids, organic substances, rhombic and monoclinic sulphur, and ice, have been made over temperature-intervals ranging from about +50° to −190°.

The results obtained for benzophenone and betol indicate that the specific heat of these substances diminishes to an abnormally large extent as the temperature is lowered. H. M. D.

Specific Heat at Low Temperatures. II. WALTHER NERNST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 262—282).—Whereas the apparatus described in the preceding abstract only permits of measurements of the mean specific heat over considerable intervals of temperature, the author has devised an entirely different type of calorimeter, by means of which true specific heats can be obtained at temperatures down to about −200°. In this form of apparatus the substance under investigation serves as the calorimeter. A thin platinum wire of high resistance is suitably embedded in the substance, which is suspended in a highly exhausted vessel. A measured quantity of electricity is sent through the wire, and the resulting change of

temperature of the surrounding substance is determined by means of the alteration in the electrical resistance of the wire. For the success of the measurements, it is absolutely essential that the thermal isolation of the substance examined should be as complete as possible, and it is recommended that the degree of exhaustion of the containing vessel should be controlled by means of an attached Geissler tube. Slight modifications in the form of the apparatus are described for the investigation of solid substances of low thermal conductivity and also of liquids.

The results of measurements made with the substances referred to in the previous abstract are recorded, and the data are used to test the thermodynamic relationship obtained by the author in an earlier paper (compare Abstr., 1906, ii, 727). The principal general result of the measurements is that the specific heat diminishes with increasing rapidity as the temperature falls. The variation is such that a convergence towards a zero value at $-273°$, as required by Einstein's theory, seems to be quite possible. H. M. D.

Specific Heat of the Elements at Low Temperatures. THEODORE W. RICHARDS and FREDERICK G. JACKSON (*Zeitsch. physikal. Chem.*, 1910, 70, 414—451).—The average specific heat of a number of elements between $-188°$ (the temperature of liquid air) and $+20°$ has been determined by the method of mixtures. The arrangements employed, which do not differ greatly from those of previous observers (compare Behn, Abstr., 1900, ii, 259; Tilden, Abstr., 1900, ii, 524), except as regards the correction for the disturbances attending the transfer of the cold substance to the calorimeter, are described in detail. With reference to the latter point there are two sources of error: (1) the cooling effect exerted on the calorimeter by the descending current of air from the cooling apparatus during the transference; (2) the warming of the substance under examination during the transference. The former effect has been found to be considerably the more important. In the case of a solid substance, both errors can be corrected for by determining the specific heat of a solid and of a hollow piece of metal the same exterior size; the difference in the cooling effects of these two pieces is due to the difference in weight, and from the results the true specific heat can readily be calculated. Similarly, a correction can be applied to materials in pieces or powder by comparing the cooling effect produced by substance and container with that produced by the container alone. The mean results are probably accurate to within a fraction of 1%.

The mean values between $-188°$ and $+20°$ referred to the 20° calorie are as follows: carbon (graphite) 0·0959; magnesium 0·208; aluminium 0·175; silicon 0·118; phosphorus 0·169; sulphur 0·131; chromium 0·0794; manganese 0·0931; iron 0·0859; nickel 0·0869; cobalt 0·0828; copper 0·0789; zinc 0·0846; arsenic 0·0705; molybdenum 0·0555; palladium 0·0517; silver 0·0511; cadmium 0·0515; tin 0·0502; antimony 0·0469; platinum 0·0279; gold 0·0297; thallium 0·0296; lead 0·0300; bismuth 0·0284.

The atomic heats at low temperatures of all the elements except those with the lowest atomic weights conform approximately to

Dulong and Petit's law, the value of the constant being 5·3. There are, however, certain deviations, and these show distinct periodicity, the general tendency being towards increasing atomic heat with increasing atomic weight.

The results are in good agreement with those of Behn (*loc. cit.*), which are regarded as the most accurate of previous observations. [Compare also Schimpf (this vol., ii, 181), whose results were published after the foregoing paper was written.] G. S.

Specific Heat and Chemical Equilibrium of Ammonia Gas. WALTHER NERNST (*Zeitsch. Elektrochem.*, 1910, **16**, 96—102).—A new method of determining the relative specific heats of gases is described. A steady current of the gas passes first through a silver-lined copper tube, the upper part of which is filled with silver foil; it then passes by a short porcelain tube into a solid cylinder of silver, in which holes are drilled in such a way that the gas passes up and down the length of the cylinder eight times before escaping by a porcelain tube. The silver cylinder and the upper part of the copper tube are enclosed in an electrically heated chamber formed of a thick-walled copper cylinder. The temperatures of the copper tube, the silver cylinder, and the chamber are all measured by thermocouples. The silver cylinder (when no gas is passing) is practically at the same temperature as the electrically heated copper cylinder, whereas the silver-filled copper tube, which projects out of the furnace, is about 200° cooler. When a current of gas is passed, it cools the silver cylinder proportionally to its specific heat and its rate of flow; the temperature of the furnace must of course be kept constant during the comparison of two gases.

In determining the specific heat of ammonia (which was found to pass through the apparatus without appreciable decomposition), steam, oxygen, and carbon dioxide were used for comparison. The mean values of the molecular heat at constant pressure found are: 365—567°, 10·4; 480—680°, 11·2. The formula $Cp = 8{\cdot}62 + 0{\cdot}0020t + 7{\cdot}2t^3 \times 10^{-9}$ represents these results, and also those of Keutel, Voller, Wiedemann, and Regnault with sufficient accuracy.

By means of this formula the heat of formation of ammonia at 850° is calculated to be 30,220 cals., a value which agrees much better with Jost's equilibrium measurements than with those of Haber and Le Rossignol, which lead to the values 28,000 and 24,000—25,600 respectively (Abstr., 1908, ii, 362).

The author's thermodynamic theorem, using the newer value 1·6 for the chemical constant of hydrogen and the value of the specific heat of ammonia now determined, is in satisfactory agreement with the equilibrium measurements. T. E.

Specific Heat of Solutions. W. F. MAGIE (*Zeitsch. physikal. Chem.*, 1910, **71**, 636).—The author points out that he has already proposed a formula (*Physical Review*, 1907, **25**, No. 3) for the specific heat of solutions of electrolytes similar to that of Bakowski (Abstr., 1909, ii, 375). G. S.

Changes of Volume and Heat Development Occurring when the Components of a Compound which Vaporises Unchanged are Transferred Separately into the Gas Space. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1910, **70**, 462—476).—A theoretical paper. In previous papers (Abstr., 1909, ii, 543, 985; this vol., ii, 194) it has been shown that the equation $r_1/s_1 = r_2/s_2$ (where r_1 and r_2 are the amounts of heat taken up by the system, and s_1 and s_2 respectively the changes of volume which occur when unit mass of the first and of the second component respectively is transferred at constant temperature and pressure from the first to the second phase) is of fundamental importance for binary systems. In the present paper the bearing of the terms in the equation is further discussed. It is shown that when a binary compound AB is in equilibrium with its dissociation products, the transfer of a mol. of A or B from the liquid to the gas space causes the same increase of volume, and requires the expenditure of the same amount of heat.

G. S.

Vapour-pressure Curves of Binary Mixtures. Remarks on Zawidzki's Paper. EMIL BOSE (*Zeitsch. physikal. Chem.*, 1910, **71**, 637—640).—An adverse criticism of van Zawidzki's theoretical treatment of the subject (compare Abstr., 1909, ii, 968). The author has repeatedly pointed out that the Margules solution functions with few coefficients, as used by Zawidzki, are not satisfactory (compare Abstr., 1909, ii, 214).

G. S.

Do Negative Vapour-pressure Curves of [Binary] Mixtures of Liquids Necessarily Imply the Existence of Molecular Compounds? DEMETRIUS E. TSAKALOTOS (*Zeitsch. physikal. Chem.*, 1910, **71**, 667—670).—The author answers this question in the negative. Although in many cases the existence of a minimum in the total vapour-pressure curve occurs in mixtures in which chemical combination is probable, such a minimum also occurs in other cases, in mixtures of formic acid and water, for example, for which there is no evidence of chemical combination.

G. S.

Vapour Pressures and Boiling Points of Mixtures of Saturated Alcohols with Water. ANTONY G. DOROSCHEWSKY and E. V. POLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 109—134).—The authors have measured the boiling points of aqueous solutions of methyl, ethyl, and propyl alcohols for concentrations increasing by 10% from 0 to 100 and at the pressures 700, 760, and 800 mm. For all the aqueous solutions of these alcohols, it is found that the ratio of the absolute boiling points at two definite pressures is constant. Thus, $T/760 : T/700 = 1{\cdot}0060$, $T/760 : T/800 = 0{\cdot}9962$, and $T/800 : T/700 = 1{\cdot}0099$, the limiting values for these three ratios being 1·0060—1·0062, 0·9960—0·9963, and 1·0096—1·0102. So that for water, saturated alcohols, and mixtures of the two at pressures near to the ordinary atmospheric pressure, the value of T/T_1 is independent of the composition, and is a function of the pressure alone. It is, therefore, possible, from the vapour pressure of an alcohol or water, to calculate

the vapour pressure of any aqueous solution of the alcohol at any temperature if the b. p. at any pressure is known. This relation also holds, as far as the available experimental data show, for the high temperatures corresponding with the critical pressures.

It was found by Wüllner (*Ann. Phys. Chem.*, 1884, 5, Erganz-bd. 11) that, for mixtures of ethyl alcohol and water, $c/(a+b)$ = const., where c, a, and b are the vapour pressure of the mixture, water, and alcohol respectively at one and the same temperature. The authors find that the value of $c/(a+b)$ for mixtures of the saturated alcohols with water depends on the kind of mixture, on the composition of the solution, and on the temperature, and that Wüllner's law applies with the same degree of accuracy to aqueous methyl and propyl alcohols as to aqueous ethyl alcohol, the value of the ratio remaining only approximately constant even at high temperatures—above 50°. With propyl alcohol the value of $c/(a+b)$ changes with the temperature in the same direction both for dilute and concentrated solutions; for methyl alcohol, however, the value increases with dilute, and diminishes with concentrated, solutions as the temperature rises. The latter is also the case with ethyl alcohol, but for the aqueous solution of this alcohol possessing a constant b. p. (95·57% solution at 760 mm.), the value of the ratio is independent of the temperature.

T. H. P.

Effect of Gravity on the Boiling Point. WILHELM SIEPERMANN (*J. pr. Chem.*, 1910, [ii], 81, 190—191).—The connexion between gravity and the b. p. of a liquid, suggested in a qualitative way by Krafft (Abstr., 1909, ii, 969), had previously been expressed quantitatively by the author in a pamphlet published in 1906. C. S.

Estimation of the Temperature and Pressure in Vacuum Distillation. CHRISTIAN JOHANNES HANSEN (*J. pr. Chem.*, 1910, [ii], 81, 282—288).—A reply to von Rechenberg (this vol., ii, 101). Rechenberg's proposal to attach the manometer to the boiling flask is untenable, since two manometers situated at different heights in the neck of the flask give different readings. The only practical way to describe the b. p. under very low pressures is to state the pressure exerted in a part of the apparatus free from vapour and the height of the vapour column in the flask. C. S.

Thermal Analysis in Metallurgical Processes. K. FRIEDRICH (*Metallurgie*, 1910, 7, 33—39).—The method of taking heating and cooling curves, employed in the study of alloys, may be extended to slags, mattes, etc., and methods of investigating metallurgical processes on these lines are described. C. H. D.

Use of the Melting-point Apparatus for Low Temperatures as a Low Temperature Bath in Physico-chemical Laboratories. H. STOLTZENBERG (*Zeitsch. physikal. Chem.*, 1910, 71, 649—651).—The melting-point apparatus for low temperatures already described (this vol., ii, 17) has been improved in some respects, and may be employed to obtain constant temperatures at any desired

point down to $-140°$. The improved apparatus is described and figured. G. S.

Optical Temperature Measurement in the Case of Polished Substances. H. VON WARTENBERG (*Ber. Deut. physikal. Ges.*, 1910, 121—127).—The melting points of several metals have been measured by means of a Wanner pyrometer, the metals being contained in an electrically heated tube of tungsten, which behaves as a black body. Taking the melting point of platinum = 1745° as standard temperature, the following numbers were obtained: iridium 2360°, rhodium 1940°, vanadium (97%) 1710°, platinum-rhodium 1830°, molybdenum $>2500°$, Nernst-lamp rod 2550°.

It is found that the formula given by Holborn and Henning for the relationship between the apparent and the true temperature of a hot substance of known absorption capacity can be used for the accurate estimation of temperatures up to the melting point of tungsten (2900°). H. M. D.

Relations between the Freezing-point Depression, Ionic Concentration, and Conductivity of Electrolytes. J. B. GOEBEL (*Zeitsch. physikal. Chem.*, 1910, **71**, 652—666. Compare Abstr., 1906, ii, 332).—The total concentration, c_r, of the particles in a solution (whether electrolyte or non-electrolyte) may be calculated from the freezing-point depression, d, by means of the equation:

$$c_r = 0{\cdot}705 \log_{10}(1+d) + 0{\cdot}24d + 0{\cdot}004d^2.$$

When the concentrations of the ions and molecules in solutions of electrolytes are calculated by means of these values, it is found that both binary and ternary electrolytes follow the law of mass action.

Binary electrolytes of the type MX, for example, which ionise according to the equation: $MX \rightleftarrows M^{\cdot} + X'$, follow the Ostwald dilution law: $c_2^2 = kc_1$, where c_1 represents the concentration of the unionised molecules and c_2 that of the ions. Similarly, for a ternary electrolyte, MX_2, which ionises according to the equations: $MX_2(c_1) \rightleftarrows MX'(c_3) + X'(c_2)$ and $MX'(c_3) \rightleftarrows M^{\cdot\cdot}(c_4) + X'(c_2)$, the values of k_1 and k_2 in the equations $c_2c_3 = k_1c_1$ and $c_2c_4 = k_2c_3$, calculated from the most trustworthy cryoscopic data by the above formula, are fairly constant, as required by the law of mass action.

From the values of the ionic concentrations, c_2, thus obtained, the molecular conductivity can be calculated. For strong binary electrolytes ($k > 0{\cdot}18$), the formula in question is $\lambda = \lambda_0 - 5{\cdot}63\sqrt{\lambda_0 c_2}$, where λ_0 is the molar conductivity at infinite dilution. For ternary electrolytes the more complicated formula: $\lambda = \lambda_2 - (\lambda_2 - \lambda_1)/[(1+38k_3)(1+c_2)]$, where $k_3 = k_1k_2$, $\lambda_1 = \lambda_0 c_2/2c$, and $\lambda_2 = \lambda_0 - 4{\cdot}8\sqrt{\lambda_0}\sqrt[3]{c_2}$, is given.

The above equations are valid between $c = 0$ and $c = 1$. G. S.

Cryoscopy in Concentrated Solutions. ÉMILE BAUD (*Compt. rend.*, 1910, **150**, 528—529).—Determinations of molecular weight in concentrated solutions can be effected if the solvent has little tendency to form associated molecules, and if the concentration is represented as weight of solute per unit volume of solution. The equation then becomes $M = wK/d$, where M is the molecular weight of the solute,

w the weight of substance per 100 c.c. of solution, and d the depression of the freezing point. The constant K has been found to have the value 54·5 for ethylene dibromide, 56·5 for benzene, and 57·9 in the case of nitrobenzene. W. O. W.

Heat of Formation of Hydrogen Iodide from the Elements. PH. STEGMÜLLER (*Zeitsch. Electrochem.*, 1910, **16**, 85—92).—Bodenstein's measurements of the equilibrium between hydrogen iodide, hydrogen, and iodine indicate that the heat of formation of hydrogen iodide changes more rapidly with temperature than the (rather uncertain) values of the specific heats of the gases would suggest. The author has therefore determined the *E.M.F.* of the cell $H_2 \mid HI \mid I_2 + HI$ and the pressures of the hydrogen iodide and iodine in the saturated vapour of the solutions used. From these data the heat of formation of gaseous hydrogen iodide from hydrogen and iodine vapour is calculated by means of Helmholtz's equation: $A = Q + T.dA/dT$, and van't Hoff's equation: $A = RT\log K - RT\log[HI]/[I_2]^{\frac{1}{2}}[H_2]^{\frac{1}{2}}$. The mean values of the heat of formation found are: at 43·4°, 2291 cals.; at 68·4°, 2758 cals.; at 56·6°, 2494 cals., with an uncertainty of several hundred calories. Thomsen's calorimetric determinations lead to the value 1500 cals., whilst Bodenstein's measurements give from 142 to 192 cals. Further experiments are required to clear up the discrepancy. T. E.

Heat of Hydration. WILLEM P. JORISSEN (*Chem. Weekblad*, 1910, **7**, 180—187. Compare Abstr., 1909, ii, 120).—An investigation of the heat of hydration of strontium chloride, $SrCl_2,2H_2O$, to $SrCl_2,6H_2O$, and a comparison of the observed values with those obtained by means of van't Hoff's formula. A. J. W.

Heats of Combustion of the Octanes and Xylenes. THEODORE W. RICHARDS and RICHARD H. JESSE, jun. (*J. Amer. Chem. Soc.*, 1910, **32**, 268—298).—Richards, Henderson, and Frevert (Abstr., 1907, ii, 604) have given an account of the determination of the heats of combustion of sucrose and benzene by means of an adiabatic method of calorimetry. The work has now been extended to several other organic compounds, the same method being adopted with slight modifications.

Regarding the heat of combustion of sucrose as 16·545 kilojoules per gram (Fischer and Wrede, Abstr., 1904, ii, 469), the molal heats of combustion of the following liquid hydrocarbons, expressed in kilojoules and determined in constant volume at 20°, have been found to have the values: benzene, 3278; *o*-xylene, 4570; *m*-xylene, 4570; *p*-xylene, 4554; *n*-octane, 5256; $\beta\epsilon$-dimethylhexane (di*iso*butyl), 5250; β-methylheptane, 5261; $\gamma\delta$-dimethylhexane, 5252; β-ethylhexane, 5247. The addition of CH_2 in aromatic compounds produces an increase in the heat of combustion amounting to 644 kilojoules, or 154 Cal. E. G.

The Heat of Coagulation of Colloidal Solutions. FRIEDRICH DOERINCKEL (*Zeitsch. anorg. Chem.*, 1910, **66**, 20—36).—Attempts to

measure the thermal changes in the coagulation of hydrosols have led to very discordant results. Hydrosols of ferric hydroxide and silicic acid have now been examined.

A platinum calorimeter and gilt copper mixing vessel are used, both enclosed in the same air-jackets. The valve in the mixing vessel consists of a plano-convex glass lens, resting on a plano-concave lens with a central hole, cemented into the base of the vessel. The valve is released by a silk thread.

In each experiment, 250 c.c. of hydrosol are mixed with 250 c.c. of the precipitating reagent. The difference between the development of heat thus observed and that found on mixing equal volumes of the precipitating reagent and pure water is taken as the heat of coagulation. The specific heat of all the solutions used is determined by means of a standard calorifer, and is found to agree with that calculated.

The results vary greatly with the concentration. In the case of a 10% ferric hydroxide hydrosol, the heat of coagulation with potassium oxalate has a maximum value for a certain concentration, in other cases the maximum is not observed. The heat-development increases with the quantity of adsorbed salt, slowly at first and then more rapidly. The coagulation of ferric hydroxide by potassium oxalate develops about three times as much heat as when aluminium sulphate is used, and the coagulation takes place more slowly in the second case There is no development of heat when the hydrosol is diluted with water. The heat of coagulation per gram of hydrosol is considerably greater in dilute than in concentrated solutions. This is probably due to the formation of hollow cells of hydrogel observed in concentrated solutions, a part of the solution thus being removed from reaction. Differences between different preparations of the same hydrosol are shown to be due to differences in the amount of contained electrolyte. C. H. D

Theory of Corresponding States. DMITRI A. GOLDHAMMER (*Zeitsch. physikal. Chem.*, 1910, **71**, 577—624).—A number of formulæ, mostly deduced from the fundamental formulæ of van der Waals on corresponding states, are tested by means of the available experimental data.

The formulæ $\rho_1 - \rho_2 = m\rho_k \sqrt[3]{1 - T/T_k}$, where m is a constant for all substances, $\rho_1 + \rho_2 - 2\rho_k = n\rho_k(1 - T/T_k)$ (Cailletet and Mathias), and $(\rho_1 - \rho_2)^3/(\rho_1 + \rho_2 - 2\rho_k) = 27\rho_k^2$, where ρ_1 and ρ_2 represent the densities of liquid and vapour respectively at the temperature T, and ρ_k is the critical density, have been tested with satisfactory results for thirty substances. The last equation has been used to calculate the critical densities for thirty-two substances, for which these magnitudes are not accurately known. The results are probably accurate to 1%.

The formula $T_k = T_2 + (T_2 - T_1)/[(\sigma_1/\sigma_2)^3 - 1]$, where $\sigma = \rho_1 - \rho_2$, may be used to calculate the critical temperature, T_k, for all substances, even for the alcohols, provided the temperature is sufficiently high.

The formulæ $\gamma = A(\rho_k/M)^{\frac{2}{3}}(1 - T/T_k)^{\frac{5}{4}}T_k$ and $\gamma[M/(\rho_1 - \rho_2)]^{\frac{2}{3}} = KT_k(1 - T/T_k)^{\frac{37}{36}}$, where γ represents the surface-tension and M the normal molecular weight, have also been tested for a large number of

substances. The first of these two formulæ is a modified form of that of Eötvös Ramsay-Shields, and is claimed to give more correct values for the molecular complexity of liquids than the latter. The degree of association for substances containing the hydroxyl group is smaller according to the above formula than by the Eötvös formula.

The formula $T_k = T_2 + (T_2 - T_1)/[(\gamma_1/\gamma_2)^{0.8} - 1]$ admits of the accurate calculation of T_k when sufficiently high temperatures are chosen. Fairly accurate values for T_k can also be obtained from observations at low temperatures when the degree of association does not alter much with the temperature.

For substances the association of which alters fairly rapidly with the temperature, an approximate value of the critical temperature T_k can be obtained by means of the formula: $T_k = T_2 + (T_2 - T_1)/[(\gamma_1/\gamma_2) - 1]$.

G. S.

Specific Volumes of the Saturated Vapours of Pure Substances. SYDNEY YOUNG (*Zeitsch. physikal. Chem.*, 1910, **70**, 620—626).—The curves representing the volume of a gram of saturated vapour at different temperatures for thirty pure substances have been reconstructed from the author's experimental data already published on principles described in the paper, and it has been found that the results already published require slight correction at low temperatures. The corrected data for the volume of a gram of saturated vapour are therefore given in tabular form at intervals of 10° from 0° to the critical temperature, and the critical temperatures and volumes of a gram are also given, as well as a list of the papers containing the original data. G. S.

Friction in Gases at Low Pressures. J. L. HOGG (*Phil. Mag.*, 1910, [vi], **19**, 376—390).—The dependence of the friction on the pressure of a gas at low pressures has been examined by measuring the logarithmic decrement of a suspended disk made to oscillate as a torsion pendulum between two fixed plates. The pressure of the gas was determined by means of a McLeod gauge. In earlier measurements, difficulties were experienced at the lowest pressures in consequence of the diffusion of comparatively large quantities of mercury vapour into the friction apparatus. This disturbing factor was eliminated by the attachment of tubes, which were cooled in liquid air. With this arrangement no mercury lines could be detected in an attached spectrum tube when the temperature of the viscosity apparatus was raised to 150°.

Experiments with pure dry hydrogen indicate that the relationship between the pressure of the gas and the logarithmic decrement is that required by Sutherland's formula. This holds for pressures between 0·1 mm. and 0·000016 mm. The proof of the validity of this formula obviously permits of pressure determinations from observations on the decrement of the oscillating disk. It also appears probable that, so far as hydrogen is concerned, the McLeod gauge can be depended on for the measurement of pressures as low as the smallest used in these experiments. H. M. D.

Absorption of Sulphur Dioxide by Caoutchouc and by Wool. ALBERT REYCHLER (*J. Chim. Phys.*, 1910, 8, 3—9).—An apparatus is described by means of which the absorption phenomena have been studied. Denoting by C and c respectively the number of mols. of sulphur dioxide per kilogram of caoutchouc and per litre of gas, it is found that the ratio C/c at 18° is constant and equal to 26·0. The absorption of sulphur dioxide by caoutchouc is therefore a simple process of solution.

In the case of fat-free wool containing 11·4% of water, the relationship between C and c is given by the equation $C = 0·88 + 44·7c$, provided that c is greater than about 0·005 mol. per litre. When the concentration of the gaseous sulphur dioxide is smaller than this, the amount of absorbed gas is less than that required by the equation, and the difference between the two quantities increases as the concentration diminishes. The observed results are considered to indicate that a part of the absorbed sulphur dioxide is chemically combined with the wool. The quantity thus combined increases at first with the concentration, but attains a maximum, represented by 0·88 mol. sulphur dioxide per kilogram of wool. H. M. D.

Colloidal Chemistry of Caoutchouc. I. Theory of Vulcanisation. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 136—155).—On the basis of published data relating to the vulcanisation of caoutchouc, an attempt is made to account for the phenomena observed in this process on the basis of the theory of adsorption. A summary of the most important results is promised in a further paper.

The rate at which sulphur is taken up by caoutchouc in the hot vulcanisation process varies less rapidly with the temperature than is the case for most chemical reactions, and this is cited as evidence in favour of the adsorption theory as opposed to the purely chemical theory of the process. H. M. D.

Fabrics and Insoluble Colouring Matters. LEO VIGNON (*Compt. rend.*, 1910, **150**, 472—474. Compare Abstr., 1909, ii, 576). —Insoluble substances, such as soot, Prussian blue, copper sulphide, or copper arsenite, are capable, when in a finely divided condition, of dyeing cotton, silk, and wool equally well. The intensity of the colour produced appears to depend mainly on the state of division of the colouring matter, since better results are obtained with the freshly precipitated substances than with those which have become granular with the lapse of time. Microscopic examination of the dyed fabric renders evident the existence of distinct granules in the case of the inorganic substances studied, whilst with insoluble organic dyes the fabric appears uniformly coloured, no granular appearance being visible. W. O. W.

Does Calomel Furnish Another Contradiction of the Theory of Heterogeneous Dissociation Equilibrium? ALEXANDER SMITH (*J. Amer. Chem. Soc.*, 1910, 32, 187—189).—It has been shown by Johnson (Abstr., 1908, ii, 157) that at 345° the dried and undried forms of ammonium chloride, although yielding undissociated and

dissociated vapour respectively, nevertheless exert equal vapour pressures (760 mm.). Abegg (*loc. cit.*) has pointed out that this result is inconsistent with the theory of heterogeneous dissociation equilibrium.

The present author states that, in view of the work of Brereton Baker (Trans., 1900, **77**, 646), mercurous chloride appears to exhibit the same anomaly, and that he is carrying out experiments on the subject. E. G.

Free Diffusion of Non-electrolytes. I. L. WILLIAM ÖHOLM (*Zeitsch. physikal. Chem.*, 1910, **70**, 378—407).—The experiments were made by the method described in a previous paper (compare Abstr., 1905, ii, 147) at temperatures in the neighbourhood of 9° and 20°. For convenience of estimation, only optically active substances were used, and the concentrations were varied widely.

In all cases the diffusion-coefficients diminished with increasing concentration. By means of the temperature-coefficients of diffusion the results were all referred to 20°, and the variations of the diffusion-coefficients for the extreme limits of concentration employed are as follows: Sucrose 0·378 to 0·275 for 0·075N to 2N; lactose 0·369 to 0·361 for 0·10N to 0·20N; maltose 0·364 to 0·328 for 0·1N to 0·5N; raffinose 0·311 to 0·297 for 0·05N to 0·25N; dextrin 0·104 to 0·0924 for 0·075N to N; arabinose, 0·569 to 0·520 for 0·1N to 0·5N; nicotine 0·456 to 0·273 for 0·1N to N. Except in two cases, the mean values of the temperature-coefficients of diffusion are about 0·033; for arabinose the value is about 0·044, and for nicotine, about 0·016.

The values of the diffusion-coefficients at infinite dilution, k_∞, are obtained from the above values by extrapolation, and when these are substituted in the expression $k_\infty\sqrt{M}$, it is found that this expression is approximately constant, the mean value being about 7. Nicotine gives a somewhat smaller value. Assuming that the same expression holds for dextrin, the molecular weight of the latter must be about 4440, and the value of n in the formula $(C_6H_{10}O_5)_n$ is 27 ± 1. G. S.

Osmotic Pressure of Concentrated Solutions of Non-Electrolytes. OTTO SACKUR (*Zeitsch. physikal. Chem.*, 1910, **70**, 477—495).—The greater part of the results described in this paper has already been published (compare Abstr., 1908, ii, 931). The vapour-pressure measurements of Zawidzki (Abstr., 1901, ii, 6) are also satisfactorily represented by the formula for all three types of curve up to osmotic pressures of 200 atmospheres.

The theory of Dolezalek (Abstr., 1909, ii, 22; this vol., ii, 184) is also discussed. Its apparent simplicity as compared with that of the author is purely algebraical. Dolezalek's theory, founded on Raoult's laws, is not susceptible of a kinetic explanation so long as no connexion is known between the molecular fractions and the volume occupied by the molecules. G. S.

Diffusive Power of Certain Artificial Colouring Matters. LÉO VIGNON (*Compt. rend.*, 1910, **150**, 619—622 *).—It is shown, from determinations of rates of diffusion in water, that dyes may be divided into two well-defined classes. The first contains substances,

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 291—294.

such as picric acid, which form true solutions, whilst the second group includes the substantive dyes of the Congo-red type. The latter form colloidal solutions, and show feeble diffusive power.

W. O. W.

Theory of Solutions. ALEXANDER A. JAKOWKIN (*Zeitsch. physikal. Chem.*, 1910, 70, 158—197).—A theoretical paper. The author considers that osmotic pressure is connected with association between solvent and solute, and shows that this assumption is compatible with the fact that dilute solutions follow the gas laws.

On the assumption that the two components A and B of a binary mixture unite reversibly to form a compound AB, as represented by the equation $A + B \rightleftarrows AB$ (1), it is shown that the ratio of the osmotic pressure P to the gas pressure G is represented by the equation $P/G = \left(\frac{N}{n} + \frac{m}{M}\right) \log. \frac{1}{x}$ (2), where M and N represent the molecular weight and the number of molecules of the solvent, and m and n the corresponding magnitudes for the solute. $1/x = p_0/p$ is the ratio of the vapour pressure of the solvent to the partial pressure of the latter in the solution, and is calculated by means of the equation :

$$kx(1 - 2y + xy) = (1 - x)(1 - y + xy),$$

obtained by applying the law of mass action to the equilibrium represented by equation (1). k is an association constant, representing the affinity between A and B. The ratio P/G is then calculated by substitution in equation (2) with different values of the affinity constant k, and it is shown that for dilute solutions the osmotic pressure is practically the same as the gas pressure if the affinity between solvent and solvent is not too small, in other words, when k is not less than 8; further, however great the affinity may be, the ratio of P to G cannot exceed 1·05.

The above result is obtained on the assumption that one molecule of the solute can bind only one molecule of the solvent. In certain cases, however, the solute may associate itself with more than one molecule of the solvent. If the solute AX is dissolved in water, the simple association already considered is represented by the equation $AX + H_2O \rightleftarrows AX,H_2O$, and the further association, setting in when the first is practically complete, by the equation :

$$AX.H_2O + m.H_2O \rightleftarrows AX.(m+1)H_2O,$$

in which a further m molecules of solvent are bound. The general equation for equilibrium in such systems is $\xi^{m+1}/v^m(1 - \xi) = \text{const.}$ (3), where ξ represents the concentration of the more highly hydrated, and $(1 - \xi)$ that of the less highly hydrated or non-hydrated form. For $m = 1$, equation (3) becomes $\xi^2/(1 - \xi)v = \text{const.}$, which is the equation for the electrolytic dissociation of a binary electrolyte, and the author suggests that the increase of osmotic pressure and the accompanying increase in the free energy due to the association of a second molecule of water lead to a diminution of free energy associated with electrolytic dissociation. Similarly, the association of a third molecule of water leads to a ternary electrolytic dissociation.

It is shown by means of the experimental data on partial vapour pressures due to the author and Makovetzki (compare Abstr., 1908, i, 753;

1909, ii, 796) (water and the ether of ethylene glycol) and of Perman (Trans., 1903, 83, 1173) (ammonia and water), that similar relationships hold for concentrated solutions.

The author illustrates his views as to the relationship of osmotic pressure and chemical affinity by means of an analogy to cannon and cannon-balls, which does not lend itself to concise description.

In conclusion, the connexion between the author's theory of solutions and that of Dolezalek (Abstr., 1909, ii, 22) is discussed.

G. S.

Rate of Dissolution of Salts. CARL L. WAGNER (*Zeitsch. physikal. Chem.*, 1910, 71, 401—436).—The rate of dissolution of a large number of salts which can be obtained in the crystalline form, mostly chlorides and sulphates, has been determined in the usual way at 25°. The results are expressed in terms of the dissolution velocity-coefficient: $A = 1/st \,.\, \log c/(c-x)$, where s is the area of the crystal surface acted on, t is the time, and c is the concentration of the saturated solution.

A number of experiments have been made with crystallised calcium sulphate. The form termed "marienglas" dissolves much more slowly than does alabaster. The rate of dissolution of gypsum is not the same on the different surfaces, but this may be due to the penetration of water into the capillary spaces between the leaflets. For the majority of the other salts, moderately constant values for A are obtained throughout an experiment.

The dissolution-constants of the salts, their diffusion-coefficients and solubility, and the thickness of the diffusion-layer calculated according to Nernst's formula are given in tabular form.

There is no relationship between the rate of dissolution of a salt and its solubility, but there is a connexion between the former factor and the product of the valencies of the ions into which the salt splits up on solution. Thus, for salts of valency product 1 (1×1), 2 (2×1), and 4 (2×2) respectively, the average dissolution-coefficients are 0·16, 0·08, and 0·034 respectively, so that the product of the dissolution coefficient and valency product is approximately a constant.

There is a connexion between the values of A and the diffusion-coefficients of the salts, as is to be anticipated on the basis of Nernst's theory, but, owing to uncertainty in the diffusion data, the exact connexion cannot be definitely determined. The results for the thickness of the diffusion layer are in good agreement with those of Brunner.

The paper contains an extended summary of the previous work on the subject.

G. S.

Reciprocal Solubility Influence. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 66, 93—94).—The reciprocal influence of boric and oxalic acids has been determined. The solubility of each acid in water is increased by addition of the other.

C. H. D.

A Slow Change in the Nature of Solutions of Certain Salts. WALTHÈRE SPRING (*Arch. Sci. phys. nat.*, 1910, [iv], **29**, 145—156; *Rec. trav. chim.*, 1910, [ii], **14**, 163—172 *).—In continuation of observations on the optical clearness of aqueous solutions of salts, it has been found that certain solutions, which showed the Tyndall effect in a very marked manner when freshly prepared four years ago, have since that time become almost optically clear. The electrical conductivity of the clarified solutions was determined, and the solutions were then evaporated to dryness and made up to the original volume with freshly distilled water. In all but one case, the freshly prepared solution was found to have a greater conductivity than the four years' old solution. The observed optical changes and conductivity differences are attributed to a partial hydrolysis of the salt in the preparation of the solution. The liberated acid is then supposed to react slowly with the hydrolysed portion of the salt, and the colloidally suspended hydroxide is thereby caused to disappear gradually.

The exceptional case referred to is that of a solution of potassium dichromate. This solution, after four years, was found to have a conductivity about twice as large as that of the freshly prepared solution. During the same interval, the reddish-yellow colour of the solution had changed to a pale yellow. It is shown that this change cannot be attributed to the conversion of the dichromate into chromate.

H. M. D.

Hydrolytic Decomposition and Neutral Salt Action. GEORGE SENTER (*Zeitsch. physikal. Chem.*, 1910, **70**, 511—518).—The experimental part of the paper has already been published (compare Proc. 1908, **24**, 89). The explanations of neutral salt action advocated by Euler (Abstr., 1900, ii, 269) and by Stieglitz (Abstr., 1908, ii, 168) are regarded as untenable. The effects in question are probably due mainly to the influence of the neutral salts on the reacting substances, and only in a secondary degree, if at all, to action on the solvent.

G. S.

Crystallisation and Dissolution in Aqueous Solutions. MAX LE BLANC and WILFRED SCHMANDT (*Zeitsch. Elektrochem.*, 1910, **16**, 114—115).—The rate at which a crystal gains or loses weight in a supersaturated or unsaturated solution has been measured on crystals of sodium chlorate and potassium dichromate and sulphate between 5° and 82°. At low temperatures the rates are different, but at higher temperatures they approach to equality or become equal. The process of dissolution is usually (arsenious acid is an exception) a case of diffusion. This appears to be the case, also, with crystallisation; the difference in speed may be due to the necessity for molecular orientation in the crystallisation process, which does not enter into the dissolution process.

T. E.

Influence of Substances in Solution on the Crystal-habit of Double Sulphates. HILDA GERHART (*Tsch. Min. Mitt.*, 1908, **28**, 347—368).—Several salts of the series $R_2'SO_4,R''SO_4,6H_2O$ (where

* and *Bull. Acad. roy. Belg.*, 1910, 11—22.

R′ = K or NH_4, and R″ = Zn, Mg, Ni, Co, Mn, Cd, Cu, or Fe) were crystallised from (1) pure aqueous solutions; (2) solutions containing free sulphuric acid; (3) solutions containing an excess of the alkali sulphate, and (4) solutions containing an excess of the heavy-metal sulphate. The distances of the faces from the centre of each crystal were determined and expressed in terms of the radius of a sphere of equal volume to that of the crystal. This gives a measure of any variation in the habit of the crystals. The results indicate that the salts of the metals Zn, Mg, Ni, Co, Mn, Cd are very closely related, but that the iron and copper salts (although closely related to one another) differ considerably from these in their behaviour. The potassium and ammonium salts are, in general, not similarly influenced. Amongst the potassium salts (other than those of copper and iron), the presence of free sulphuric acid has an effect only in the case of zinc potassium sulphate, there being an increase in the number of faces on the crystals; excess of potassium sulphate causes a flattening parallel to the basal plane, whilst excess of the heavy-metal sulphate has the opposite effect, namely, an elongation of the crystal in the direction of the vertical axis, together with a reduction in the number of faces. With the ammonium salts (other than those of copper and iron), the presence of free acid has little or no effect; excess of ammonium sulphate favours richness of faces, especially in the prism zone, and a flattening parallel to the orthodome; excess of the heavy-metal sulphate produces in the magnesium and manganese salts an appreciable elongation in the direction of the vertical axis, and in the nickel and cobalt salts an impoverishment of faces. With the copper and iron salts the effects of the different substances in solution are rather more marked and in other directions. L. J. S.

Formation of Disperse Systems by Metals under the Influence of Ultra-violet Light and Röntgen Rays. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 129—136).—It has been found that certain metals when immersed in water, or methyl or ethyl alcohol, and subjected to the action of ultra-violet or Röntgen rays give rise to colloidal solutions of the metals. This property is exhibited by lead, silver, tin, and copper, but not by gold, platinum, or aluminium. The effect is greatly diminished if the active metals are superficially oxidised. The quantity of the colloidal metal formed is proportional to the amount of radiation which falls on the surface of the metal. The mean size of the colloidal particles increases with increase in the time of exposure to the active rays; this is said to be due to an aggregation of the very small particles, which are formed primarily, under the influence of the active radiation. The formation of the colloidal metal is unchanged when the metal is electrically charged. For a given metal the magnitude of the disintegrating effect is dependent on the nature of the dispersive medium in which the metal is immersed. It is much greater for ethyl alcohol than for ethyl ether. An exact comparison of the behaviour of different media is, however, rendered difficult by the fact that these absorb the ultra-violet rays to very different extents.

An examination of the dependence of the effect on the wave-length

of the incident radiation indicates that colloid formation is not produced to any sensible extent by rays of wave-lengths greater than about 405 to 410$\mu\mu$.

The observed phenomena are supposed to be due to the solvent action of the liquid on the metal, whereby small quantities of a chemical compound are formed; under the influence of the ultra-violet or Röntgen rays, this compound is decomposed, and the metal separates in the colloidal form.

In support of this explanation, experiments are described which show that similar colloidal solutions are obtained when disks of the active metals are suspended immediately above the surfaces of the dispersive liquids and subjected to the action of the rays from a quartz mercury lamp. With lead and ethyl alcohol, the formation of a colloidal solution can be detected at the end of fifteen minutes. The author supposes that the metal is acted on by the alcohol vapour, and that the resulting compound dissolves in the liquid. H. M. D.

Hydrosol and Hydrogel Formation. III. ALFRED LOTTERMOSER (*Zeitsch. physikal. Chem.*, 1910, **70**, 239—248. Compare Abstr., 1907, ii, 851; 1908, ii, 364).—Buxton and Teague (compare Abstr., 1906, ii, 840, 841) have observed that when solutions of certain electrolytes in varying concentration are added to certain colloidal solutions, precipitation occurs within certain definite limits of concentration of the electrolyte, and more or less concentrated solutions may cause no precipitation. Buxton and Teague suggested a number of explanations for such phenomena, among others one referring to the dependence of the stability of colloids in the hydrosol form on the presence of ions acting as nuclei. The author suggests that all Buxton and Teague's results can readily be accounted for by means of the latter hypothesis alone, and illustrates this by reference to his own experiments on hydrosol and hydrogel formation with silver nitrate and potassium iodide (*loc. cit.*).

When potassium iodide is slowly added to silver nitrate and the latter is in slight excess, a stable, positively-charged hydrosol is formed, the $Ag^{\cdot}$ ions acting as nuclei. When sufficient iodide is added to remove the $Ag^{\cdot}$ ions, coagulation at once occurs. If, however, excess of potassium iodide is added rapidly, there is no coagulation, as the excess of I' ions then forms nuclei for the colloidal molecules.

A number of further experiments with these reagents are described. The results show that coagulation (gel formation) occurs most readily, independent of the silver iodide (hydrogel) concentration, when the hydrosol-forming ions are present in equivalent amount, and, further, that coagulation occurs the more readily the smaller the proportion of hydrosol-forming ions present in comparison with the silver iodide.

G. S.

Heterogeneous Equilibrium in Dissociating Compounds. II. F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1910, **71**, 671—704).—A more detailed account of work already published (compare Abstr., 1909, ii, 985). The present paper is mainly concerned with the equilibria in the system NH_3–H_2S, which have been fully investigated

quantitatively. The most remarkable point in connexion with the system is that in the mixture containing the components in molar proportions, the maximum sublimation point is at 88·4° and 19 atmospheres pressure, whilst the minimum melting point occurs at 116—117° at a pressure exceeding 150 atmospheres. G. S.

Existence of the Argento-argenti ($Ag + Ag^{\cdot} \rightleftarrows Ag_2^{\cdot}$) Equilibrium. Karl Jellinek (*Zeitsch. physikal. Chem.*, 1900, **71**, 513—528).—The investigations of Luther (Abstr., 1910, ii, 181), Bose (compare Abstr., 1907, ii, 735), and others having made it probable that an equilibrium of the type Ag(metal) + $Ag^{\cdot} \rightleftarrows Ag_2^{\cdot}$ exists, the author has attempted to determine the position of the equilibrium by shaking solutions of silver nitrate with finely-divided silver for prolonged periods and then analysing the solution. The glass vessels containing the solutions were either evacuated or filled with nitrogen, and experiments were made in the dark and also with artificial light.

In a few experiments at 100° in which a large amount of finely-divided silver was used, the increase of the titre of the solution was such that about 10% of the silver must have been present in the $Ag_2^{\cdot}$ form, but it was not found possible to reproduce these results. The failure is ascribed to the absence of a catalyst, which was probably present in traces in the experiments first mentioned.

The effect of catalysts, such as platinum, platinum chloride, copper, nickel, and lead nitrates, has also been tried, and in many cases the titre of the solution was diminished. It has not so far been determined in what form the silver was removed from the solution.

Circulation experiments by Bose's method (*loc. cit.*) did not lead to very definite results. G. S.

Calculation of Reaction Velocities from Current Potential Curves. Arnold Eucken (*Zeitsch. physikal. Chem.*, 1910, **71**, 550—562).—An equation is deduced by means of which the velocity of combination of a substance formed at the electrode with a substance in the solution can be calculated from observations of the current-strength in the presence and absence of the second substance. For the purposes of the calculation, the velocity of diffusion and also the thickness of the diffusion-layer for each electrode must be known; the latter is calculated from the limiting value of the current in acid solution in the usual way.

The formula has been tested with satisfactory results by means of experiments in which a solution of potassium chloride is electrolysed, and the OH′ ions which are formed at the cathode are used in hydrolysing methyl formate. This result serves to confirm the conclusions as to the great velocity of dissociation of the complex ions of certain metals already communicated (compare Abstr., 1908, ii, 1008); the statement that the velocity of dissociation of complex copper-cyanogen ions can be measured in this way is, however, erroneous.

The method may be used to measure reaction velocities of which the absolute values of the velocity constant lie between 1000 and 10^{18}.

G. S.

New Method for the Measurement of Great Reaction and Admixture Velocities. CARL BENEDICKS (*Zeitsch. physikal. Chem.*, 1910, 70, 12—27. Compare Abegg and Neustadt, Abstr., 1908, ii, 162).—The arrangement described was designed with the object of measuring high reaction velocities, such as the rate of neutralisation of acid by alkali in alcoholic solution at low temperatures, and the principle employed is to bring two small quantities of liquid together as rapidly as possible and to register photographically the rate of change of conductivity of the mixed solutions. In this connexion, an arrangement for the production of a very regular alternating current is described, and a mathematical investigation is given of the conditions under which rapid changes of conductivity are properly reproduced by the form of galvanometer used for registration.

The mixing arrangement consisted of two object glasses, in each of which round holes 9 mm. in diameter were bored, and by means of platinum foil fixed to one side of each of the glasses, small chambers were constructed which served to hold the solutions. The glasses were so placed that by the action of a spring worked by the registering apparatus itself, the two small chambers were brought together; and the mixing of the liquids is greatly accelerated by the convection currents set up by the rapid motion. When a solution is in one compartment and the solvent in another, the apparatus registers the rate of mixing; when one compartment contains an acid and the other an alkaline solution, the curve gives the time taken for complete admixture and neutralisation.

At 18°, about 0·5 second was required for the complete admixture of alcohol and an alcoholic solution of lithium hydroxide, whilst the complete admixture and neutralisation of alcoholic solutions of lithium hydroxide and hydrogen chloride required only 0·2 second. It is pointed out that unless lowering of temperature diminishes the velocity of neutralisation to a much greater extent than the velocity of admixture, which is very doubtful, such measurements may be carried out most successfully at the ordinary temperature. G. S.

Velocities of Certain Reactions between Metals and Dissolved Halogens. RALPH G. VAN NAME and GRAHAM EDGAR (*Amer. J. Sci.*, 1910, [4], 237—255).—The rates of dissolution of mercury, cadmium, zinc, copper, and silver in aqueous solutions of iodine containing a large excess of potassium iodide have been measured at 25° by the usual method, and are shown to be practically equal, as would be anticipated according to the diffusion theory of Nernst (compare Abstr., 1904, ii, 315). The agreement for copper and silver is not quite so good as for the other three metals, but this is probably due to the difficulty of keeping the surfaces of the two former metals free from solid iodine. The temperature-coefficient of the reaction for 10° between 25° and 35° is about 1·3. Increase of the potassium iodide concentration accelerates the reactions, and as qualitative experiments appear to indicate that iodine (or rather the compound KI_3) diffuses more rapidly in concentrated than in dilute solutions of potassium iodide, this lends further support to the diffusion explanation of the results.

Mercury dissolves in bromine in the presence of potassium bromide slightly faster than in iodine, but in cupric bromide much more slowly, the ratio of the velocities being about 12·3 : 11·0 : 6·9.

The rate of reaction is approximately proportional to the 4/5 power of the rate of stirring. G. S.

Influence of the Medium on the Reaction Velocity and the Chemical Equilibrium. STEFAN BUGARSZKY (*Zeitsch. physikal. Chem.*, 1910, **71**, 705—759. Compare Abstr., 1902, ii, 9; 1904, ii, 551).—The velocity of the reaction between ethyl alcohol and bromine in water, carbon tetrachloride, carbon disulphide, and monobromobenzene has been measured at 25°. Particular attention was devoted to the purification of the organic solvents. In all the experiments, in which both the alcohol and bromine were used in very dilute solution, the former was in considerable excess.

In the organic solvents, the results are complicated by the removal of part of the bromine as HBr_3 by the hydrogen bromide formed in the course of the reaction, but when allowance is made for this, it is found that the rate of the reaction is proportional to the bromine concentration and between the first and second power of the alcohol concentration. The latter observation is ascribed to the presence of double molecules of alcohol in the solution, and the data are satisfactorily represented on the assumption that the main reaction takes place between the bromine and the double molecules of alcohol. In the course of the experiments, the degree of complexity of the alcohol and the dissociation constants of the compound HBr_3 in the organic solvents have been determined.

In aqueous solution at 25°, the constants calculated according to the unimolecular formula increased somewhat during the reaction. It is shown that in this case acetic acid is formed as well as acetaldehyde, and that two successive changes take place, represented by the equations: $C_2H_5{\cdot}OH + Br_2 \longrightarrow CH_3{\cdot}CHO + 2HBr$ and

$$CH_3{\cdot}CHO + Br_2 + H_2O \longrightarrow CH_3{\cdot}CO_2H + 2HBr,$$

the latter being the more rapid. A little ethyl acetate is also formed in the course of the reaction.

The velocity coefficients of the reactions in the organic solvents at 20° are as follows: carbon tetrachloride, 0·00420; carbon disulphide, 0·00922; bromobenzene, 0·0300; and in water at 25°, 0·00575. It is suggested that in the last case the reaction takes place between bromine and hydrated alcohol molecules.

The distribution coefficients both of the alcohol and of the bromine between water and the organic solvents have been determined. When the velocity constants are expressed in equilibrium concentrations on the basis of the distribution measurements, the values are: carbon tetrachloride, 0·000128; carbon disulphide, 0·000122; bromobenzene, 0·00133. The conclusion which might be drawn from the first two numbers, that the velocity of reaction of bromine on alcohol is the same in solutions which are in distribution equilibrium with one and the same aqueous phase, is rendered uncertain by the much greater velocity in bromobenzene, but there is evidence that the latter solvent plays a direct part in the reaction. G. S.

Mechanism of the Action of Bromine on Formic Acid in Aqueous Solution. GUSTAV BOGNÁR (*Zeitsch. physikal. Chem.*, 1910, 71, 529—549).—When bromine acts on formic acid in aqueous solution, the products are hydrogen bromide and carbon dioxide only. The order of the reaction cannot be determined by the usual methods owing to two disturbing causes, but measurements in the presence of hydrobromic acid at 25° show that the velocity is proportional to the concentration of the bromine and the formic acid respectively, so that the chemical change is represented by the equation :

$$H{\cdot}COOH + Br_2 = 2HBr + CO_2.$$

The disturbing causes in the simple reaction are (1) the diminution in the concentration of free bromine, due to combination to HBr_3 with the hydrogen bromide formed in the course of the reaction ; (2) the effect of the hydrogen bromide in driving back the ionisation of the formic acid, and thus diminishing the concentration of the $HCOO'$ ions. Mathematical formulæ, taking account of these disturbing causes, are deduced, it being assumed that only the $HCOO'$ ion, and not non-ionised formic acid, reacts with bromine, and are found to represent the experimental results satisfactorily. G. S.

Catalysis. Reduction of the Nitro-group by Hydrogen Sulphide. HEINRICH GOLDSCHMIDT and HALFDAN LARSEN (*Zeitsch. physikal. Chem.*, 1910, 71, 437—512).—Measurements were made with the sodium and potassium salts of *o*-, *m*-, and *p*-nitrobenzoic acids, of *m*-nitrobenzenesulphonic acid, and of *p*-nitrotoluenesulphonic acid, also with *m*-nitrophenyltrimethylammonium chloride and bromide. As hydrogen sulphide alone does not reduce nitro-compounds, alkali hydrogen sulphides had also to be used. The rate of reaction was followed by removing a small quantity of the mixture, boiling with dilute hydrochloric acid, adding excess of an acid solution of stannous chloride, warming for some time, and then titrating back with iodine. A method for working with hydrogen sulphide under increased pressure is described. The nature of the equilibrium in hydrosulphide solutions saturated with hydrogen sulphide has been investigated.

The chief products of the reduction of the nitro-compounds mentioned above, by means of acid sulphide and hydrogen sulphide, are hydroxylamino-compounds; m-nitrobenzoic acid, for example, gives *m*-hydroxylaminobenzoic acid, $OH{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$. Amino-compounds are also formed in small amount. The rate of the reaction is approximately proportional to the acid sulphide concentration, and almost independent of the hydrogen sulphide concentration. For salts of nitrated bases, the reaction is approximately unimolecular; the rate is diminished by the addition of electrolytes with a common ion. The reduction of salts of nitrated acids is represented in some cases satisfactorily by the more complicated equation: $kct = \log_e a/(a - x) - \log_e(a + b)/(a + b - x)$, where the symbols have the usual significance. The complications in the reaction velocity in this case are probably due to polysulphides. The addition of electrolytes with a common ion accelerates reactions of this type.

The reduction of nitro-compounds by sulphides or polysulphides in the absence of hydrogen sulphide leads mainly to the production of

amino-compounds according to the equation: $4RNO_2 + 6Na_2S + 7H_2O = 4R\cdot NH_2 + 3Na_2S_2O_3 + 6NaOH$. The thiosulphate is not, however, a primary product of the reaction, but is produced by interaction of polysulphides and hydroxides.

The mechanism of the reactions has not been thoroughly elucidated. It is probable that some of the deviations from the simple laws are due to the action of polysulphides.

One possible explanation of the independence of the reduction velocity of the hydrosulphide concentration is that both hydrogen sulphide and alkali polysulphide take part in the reduction, the latter probably by forming an easily reduced double compound with the nitro-compound. As the polysulphide concentration is inversely as the hydrogen sulphide concentration, the rate of reduction is thus apparently independent of the hydrogen sulphide concentration. Other possible explanations are also adduced. G. S.

Ester Formation with Weak Acids as Catalysts. HEINRICH GOLDSCHMIDT [and OLAF UDBY] (*Zeitsch. physikal. Chem.*, 1910, **70**, 627—643. Compare Abstr., 1909, ii, 129).—In the first part of the paper, the equilibrium between alcohol, water, and catalyst (in this case a weak acid) is discussed, and the usual assumption is made that the catalyst may form both a hydrate and alcoholate, both of which are present partly as ions, partly as non-ionised complex. Differential equations expressing the rate of the reaction are then deduced on different assumptions as to the mechanism of the reaction, it being provisionally assumed that it is the complex of alcohol and catalyst which enters into reaction with the acid to be esterified. The question mainly dealt with is whether it is the non-ionised complex of catalyst and alcohol or its ions which react with the acid.

The rate of esterification of acetic acid, *n*-butyric acid, phenylacetic acid, and formic acid in alcohol dried with calcium has been measured at 25°, trichlorobutyric acid being used as catalyst. In all cases the velocity-coefficients calculated for a reaction of the first order fall off as the action progresses, no doubt owing to the influence of the water formed in the course of the reaction. The retarding effect is much smaller than when hydrogen chloride is used as catalyst. It would be anticipated that the velocity constants would be in the ratio of the square roots of the concentrations of the acid used as catalyst; for a concentration ratio of 2 : 1, the constants should be in the ratio 1·414 : 1, but they are much greater, varying for the different acids from 1·53 to 1·81. So far, no explanation of this observation has been found.

Similar experiments to the above have also been made in the presence of the aniline salt. Up to a concentration of 0·02 normal salt, the rate of reaction is retarded, but addition of more salt has practically no effect. This shows that the non-ionised complex is concerned in the change, as the concentration of aniline salt used must reduce the concentration of the ions almost to zero.

Although water retards the ordinary reaction, it has practically no effect when a salt is also present, and it is therefore assumed that water does not affect the reaction in which the non-ionised complex is

concerned. These considerations are applied to certain reactions of similar type which have been previously investigated by the author.

G. S.

Theory of Catalytic Phenomena. D. X. ZAVRIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 36—39).—The author discusses the analogy between certain catalytic phenomena and the setting of such substances as gypsum. According to Le Chatelier, the latter action is based on the fact that burnt gypsum (hemi-hydrated) is five times more soluble than the dihydrated salt. The presence of an insufficient proportion of water to dissolve the whole of the gypsum determines the formation of a saturated solution of the hemi-hydrated salt, which is supersaturated with respect to the dihydrate, the latter being formed in the solution and immediately separated. A fresh quantity of the hemi-hydrate is then dissolved in the water, and so on, this process proceeding uninterruptedly until the whole of the gypsum is converted into the dihydrate. The water plays two parts, forming a compound with the gypsum and acting as a catalyst, by means of which the system passes from one condition into another.

The author regards this process as similar to the formation of calcium carbonate from lime and carbon dioxide in presence of a trace of moisture. A saturated solution of calcium hydroxide and carbon dioxide is formed, and this, being supersaturated with respect to calcium carbonate, deposits the latter; the water thus liberated then taking up fresh quantities of calcium hydroxide and carbon dioxide, and so on. Similarly, spongy platinum dissolves both hydrogen and oxygen, but the water produced forms, as it were, a supersaturated solution in the platinum, and is hence deposited. The decomposition of ammonium chloride in presence of moisture into ammonia and hydrogen chloride at high temperatures, and its formation from these constituents at low temperatures, are discussed from the same point of view.

The existence of thin films of moisture on the walls of glass vessels and the accompanying lowering of the vapour pressure of the water vapour are regarded as due to the probable formation of a solution of the water in the glass, the extraordinary hygroscopic character of glass being readily explained in this way.

T. H. P.

Inorganic Ferments. V. Schardinger's Reaction and Similar Enzyme Catalyses. GEORG BREDIG and FRITZ SOMMER (*Zeitsch. physikal. Chem.*, 1910, **70**, 34—65. Compare Brossa (Abstr., 1909, ii, 389; Schardinger, *Chem. Zeit.*, 1904, **28**, 704).—Schardinger has found that unboiled milk contains an enzyme which enormously accelerates the reduction of methylene-blue by formaldehyde at 70°, and the authors now show that the same reaction is powerfully accelerated by colloidal platinum and iridium, and slightly by colloidal palladium and colloidal gold. At 95°, the latter two solutions exert a very considerable, colloidal silver a slight, catalytic effect. For all colloidal metals the effect is much greater in alkaline solution.

The reaction with colloidal platinum has been investigated in detail. The velocity is greatly reduced when the formaldehyde is present in

great concentration relatively to the colloidal metal. The catalytic action of platinum is in this, as in other reactions, greatly retarded by certain "poisons," such as hydrocyanic acid, mercuric chloride, and hydrogen sulphide. Sodium formate greatly accelerates the reaction in the presence of platinum. In the latter reaction carbon dioxide is produced, probably owing to the oxidation of the formaldehyde. There is no evidence as to the oxidation products of formaldehyde when milk is used as catalytic agent.

In the presence of certain colloidal metals, methylene-blue is also rapidly reduced by free formic acid. The rate of the reaction at 25° has been measured by estimating the methylene-blue from time to time by a method due to Bernthsen (Abstr., 1886, 53; 1889, 775), depending on the use of stannous and ferric chlorides. As chlorides retard the reaction, the sulphate of methylene-blue was used for the measurements.

In this case, also, the reaction is exceedingly slow when the platinum concentration is relatively small, but above a definite relative concentration the velocity increases rapidly with increasing concentration of platinum. The action is retarded by acids, but accelerated by sodium formate. Traces of silver chloride, iodine, potassium cyanide, hydrogen sulphide, and other substances exert a powerful retarding action. Between 15° and 35°, the rate of the reaction is doubled for a rise of temperature of 10°.

Colloidal palladium, gold, and iridium also exert a catalytic effect on the reaction. Analogies are pointed out between the above reactions and those attending respiration in plants and animals. G. S.

Practical Method for the Calculation of Atomic Weights, Results obtained by its Use, and Some Deductions Drawn from it. GUSTAV D. HINRICHS (*Mon. Sci.*, 1909, [iv], **23**, 731—744).—A condensed summary of results given already in Abstr., 1906, ii, 661; 1907, ii, 945; 1908, ii, 573, 1027; 1909, ii, 653, 723; 1910, ii, 26. Notes are also given on the atomic weight data available regarding various groups of elements and the experimental conditions which should govern atomic weight determinations in the future.

T. A. H.

Kinds of Isomerism. HUGO R. KRUYT (*Ber.*, 1910, **43**, 540—545).—A theoretical paper, in which the suggestion is advanced to classify cases of isomerism, using the term in its widest sense, by the aid of the phase rule. Three classes are suggested: (*a*) two phases of one component (phase isomerism), (*b*) two components (component isomerism), (*c*) two pseudo-components (dynamic isomerism). These three classes correspond respectively with those designated by the terms physical isomerism, chemical isomerism, and tautomerism. The ideas are developed and briefly illustrated by examples. C. S.

Reversible Sulphuric Acid Tower for Drying Large Volumes of Gases. PFEIFFER (*Chem. Zeit.*, 1910, **34**, 142).—The object of the apparatus is to dry large volumes of gases with a minimum quantity of sulphuric acid.

It consists of a large and wide drying tower, on to the neck of which a second inverted tower of like form and size fits air-tight, the whole being filled with glass beads. Sulphuric acid is introduced into the lower part of the bottom tower, and the apparatus is then turned upside down, thus moistening the beads. After the gas has been passing for some time, the position of the two towers is reversed, and this manipulation is repeated at intervals. L. DE K.

Extraction of Large Quantities of Heavy Liquids with Small Quantities of Light Solvents. HERMANN EMDE (*Apoth. Zeit.*, 1909, **24**, 663).—The method depends on allowing a heavy liquid, such as a fruit juice or a plant extract, to fall, drop by drop, through a light solvent, such as ether, whereby any constituents soluble in the ether pass into the latter. The apparatus used consists of an ordinary cylindrical separating funnel, the outlet tube of which is bent four times at right angles, forming a double-hanger-shaped tube, the long limb of which is parallel with the bulb of the separating funnel. The solvent is placed in the latter to a height slightly above the upper level of the bent outlet tube, the tap being closed. The mouth of the funnel is placed under the reservoir of liquid, and the outflow from the latter is regulated by a pinchcock to small drops. The tap of the separating funnel is then turned to permit of an outflow equivalent in amount to the inflow of liquid. The process once started goes on automatically, and by the use of several separating funnels in succession, the complete extraction of large quantities of liquid can be readily accomplished. T. A. H.

A Carrier for Filled Basins or Beakers. J. EDMOND APS (*Chem. Zeit.*, 1910, **34**, 151).—A wire ring with three suspending wires, for carrying vessels filled with liquid without shaking.
C. H. D.

Inorganic Chemistry.

Behaviour of Dry Nascent Hydrogen. ALEXANDER CH. VOURNASOS (*Compt. rend.*, 1910, 150, 464—465).—Dry nascent hydrogen combines with phosphorus, sulphur, or arsenic at 400° to form the hydrides of these elements. Combination is effected by passing the vapour of the element over heated sodium formate, or by heating a mixture of sodium formate and sodium hydroxide with the element in a current of hydrogen. Under these conditions, sodium formate and sodium antimonite gave small quantities of hydrogen antimonide.

Silicon does not yield the hydride, but small quantities are obtained when silicon chloride or sulphide are employed.

Ammonia, hydrogen cyanide, and acetylene have been obtained by heating an alkali nitrate, cyanide, or carbide with sodium formate.

W. O. W.

Preparation of Perchloric Acid from Sodium Perchlorate. FRANK C. MATHERS (*J. Amer. Chem. Soc.*, 1910, 32, 66—71).—Kreider (Abstr., 1895, ii, 444) has described a method for preparing perchloric acid by the action of concentrated hydrochloric acid on dry sodium perchlorate. The present investigation was undertaken with the object of ascertaining the best conditions and the most suitable proportions of the reagents to use in order to secure the most satisfactory results. It has been found that a yield amounting to 95% of the theoretical can be obtained in the following manner: Concentrated hydrochloric acid (25—30 c.c.) is added to sodium perchlorate (20 grams); the sodium chloride is collected on an asbestos filter, and washed with ten successive portions of hydrochloric acid, each of 1 c.c.; the filtrate and washings are heated to 135° in order to expel the hydrochloric acid. The perchloric acid thus obtained is free from chlorides, but contains about 4% of sodium perchlorate. This method cannot be used with potassium or barium perchlorate.

E. G.

The Luminescence of Ozone. M. BEGER (*Zeitsch. Elektrochem.*, 1910, 16, 76).—When ozonised oxygen is heated to 350°, a phosphorescent light is seen. The decomposition of the vapour of liquid ozone, in contact with a hot glass rod for example, gives a much stronger phosphorescence.

T. E.

Compounds of Selenium with Chlorine and Bromine. ERNST BECKMANN [with RUD. HANSLIAN] (*Zeitsch. physikal. Chem.*, 1910, 70, 1—11).—The preparation and properties of selenium chloride, Se_2Cl_2, and of selenium tetrachloride, $SeCl_4$, are described. No evidence has been obtained of the existence of a compound of the formula $SeCl_2$.

When selenium and chlorine are brought together in molar proportions at $-80°$, and the mixture is allowed to warm up to room temperature and then heated to 100°, both the chloride, Se_2Cl_2, and the tetrachloride are formed. The former is a clear reddish-brown liquid, which decomposes to a considerable extent even when distilled in a vacuum, the solid tetrachloride being found in the distillate and free selenium in the retort. The chloride, Se_2Cl_2, does not solidify even at $-78°$. The action of a large excess of chlorine on the chloride leads to the formation of the tetrachloride only.

When selenium and chlorine are brought together in proportions required to form $SeCl_2$, the product is a mixture of Se_2Cl_2 and the tetrachloride.

It has already been shown (compare Abstr., 1909, ii, 137) by cryoscopic determinations in ethylene dibromide that the molecular weight of the lower chloride corresponds with the formula Se_2Cl_2. No suitable solvent for the tetrachloride has been found. The action of water on the chlorides is represented by the equations:

$2Se_2Cl_2 + 2H_2O = SeO_2 + 3Se + 4HCl$ and $SeCl_4 + 2H_2O = SeO_2 + 4HCl$.

The action of boiling bromine on selenium leads to the formation of the compounds Se_2Br_2 and $SeBr_4$. Ebullioscopic determinations with selenium in boiling bromine did not lead to very definite conclusions.

G. S.

Atomic Weight of Phosphorus. I. Analysis of Silver Phosphate. GREGORY P. BAXTER and GRINNELL JONES (*J. Amer. Chem. Soc.*, 1910, **32**, 298—318; *Zeitsch. anorg. Chem.*, 1910, **66**, 97—121).—A summary is given of previous work on the atomic weight of phosphorus. Owing to the divergence in the results recorded, it was considered desirable to undertake the re-determination of the constant.

In the present paper, an account is given of the preparation of pure silver phosphate and its analysis. The methods employed and the precautions observed are described in detail. The salt has been prepared by the interaction of silver nitrate with sodium and ammonium phosphates. Since it cannot be purified by recrystallisation, the conditions of precipitation have been so adjusted that the salt can be obtained directly in a pure state. The salt may be dried by heating it in a current of dry air. It has been found that silver phosphate does not adsorb air to a significant extent, and that it has D_4^{25} 6·37.

Four samples of silver phosphate were prepared for analysis, of which two were obtained by means of disodium hydrogen phosphate, and the others by means of disodium ammonium phosphate and sodium ammonium hydrogen phosphate respectively. The analysis was effected by dissolving the salt in nitric acid, diluting the solution with water, and pouring it into a slight excess of dilute hydrobromic acid. The precipitated silver bromide was collected and weighed, the quantity remaining in the filtrate and washings being estimated with the nephelometer.

From the average result of nine analyses, the ratio $3AgBr : Ag_3PO_4$ has been found to be 1·34562, which, assuming that Ag = 107·88 and that silver bromide contains 57·4453% of silver, leads to the value 31·04 for the atomic weight of phosphorus.

E. G.

Allotropic Forms of Phosphorus. ALFRED STOCK (*Chem. Zeit.*, 1910, **34**, 254—255).—The author does not agree with Cohen and Olie's conclusions (Abstr., 1909, ii, 998) that there are only two varieties of phosphorus, namely, yellow and metallic, red phosphorus being a solid solution of yellow phosphorus in the metallic form. If this were so, the density of ordinary red phosphorus would point to it containing 30% of the yellow variety, which would not be in accordance with its chemical and physical behaviour. All the phenomena observed by Cohen and Olie can be explained on the assumption that ordinary red phosphorus is a solid solution of several varieties of red phosphorus in each other (compare Stock and Gomolka, this vol., ii, 30).

The terms "yellow" and "metallic" should be replaced by "colourless" and "Hittorf's," since the former variety of phosphorus is colourless when pure, and the latter does not possess metallic properties.

T. S. P.

Transformation of Phosphorus in the Cardioid Ultramicroscope. H. SIEDENTOPF (*Ber.*, 1910, **43**, 692—694).—When white phosphorus, either as the solid or dissolved in carbon disulphide, is placed in the quartz cell of the new cardioid ultramicroscope, the field of view is at first quite dark. Almost immediately, however, white, sub-microscopic points are formed, which gradually increase in size and brightness, finally becoming red in colour. In the change from white to red phosphorus, there is therefore an intermediate colloidal phase formed.

The photochemical reduction of potassium dichromate and potassium permanganate also takes place rapidly in the ultramicroscope. With the latter compound, colloidal manganese dioxide is formed as an intermediate product. T. S. P.

Adsorption of Arsenious Acid by Ferric Hydroxide. ALBERT REYCHLER (*J. Chim. Phys.*, 1910, **8**, 10—11. Compare this vol., ii, 104).—Polemical against Biltz (this vol., ii, 106). The author maintains the correctness of his view, that the removal of arsenious acid from solution by ferric hydroxide is due to the formation of a hydrolysed ferric arsenite. H. M. D.

The Equilibrium in the Formation of Carbon Disulphide. F. KOREF (*Zeitsch. anorg. Chem.*, 1910, **66**, 73—92).—The reaction $C+S_2 \rightleftarrows CS_2$ has been studied at 800—1100°, within which range sulphur is diatomic, by passing carbon disulphide vapour through a heated tube, and also by passing sulphur vapour over heated Acheson graphite. Purified nitrogen was used to sweep the products through the apparatus. Tight joints are made by connecting the porcelain and glass tubes together with asbestos packing, and enclosing in an iron tube containing molten lead. Another form of very tight joint is made by packing the space between the glass and porcelain tubes with a mixture of ground porcelain and sodium silicate, drying slowly, coating externally with a thin layer of platinum, and depositing a sufficiently thick layer of silver by electrolysis.

Sulphur and carbon disulphide are condensed by means of ether and carbon disulphide. In the decomposition experiments, the values of the dissociation constant fall with time. This is shown to be due to the formation of silicon sulphide, SiS_2, in the tube, which then acts as a sulphur carrier, re-converting the carbon set free into carbon disulphide. $100K = 17{\cdot}9$ at 1009° and 25·8 at 1110°. The heat of formation C (amorph.) $+ S_2$ (gas.) $= CS_2$ (gas.) $+ 12{,}500$ cal., and using Thomsen's value for C (amorph.) + 2S (solid) = CS_2(gas.) $- 26{,}000$ cal., the value for the volatilisation of 2S (solid) is found to be $-38{,}500$ cal. Other experimental values are examined and compared. C. H. D.

The Separation of Silicon from Silicates and the Possibility of obtaining Aluminium from Aluminium Silicates. KARL GRÖPPEL (*Metallurgie*, 1910, **7**, 59—63. Compare Moldenhauer, Abstr., 1909, ii, 239).—By heating aluminium silicates with silica

and carbon in the electric furnace, silicon is obtained, the final slag having the composition $SiO_2,6—7Al_2O_3$. About 3% of cryolite renders the slag sufficiently fluid. The product does not contain more silica than bauxite, and may therefore be utilised for the production of aluminium. C. H. D.

Helium in the Air of Naples and in Vesuvius. ARNALDO PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 203—217).—The author finds that it is possible to observe the D_3 helium line in 3·5 c.c. of the air of Naples. Zircon from Vesuvius also contains a small proportion of helium, its density being low and its radioactivity high. Examination of samples of zircon from other sources shows that these form two groups, possessing (1) high content of helium, high radioactivity, and low density, and (2) low content of helium, low radioactivity, and high density. T. H. P.

True Atomic Weights. Stas' Determinations. III. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1910, [iv], **7**, 119—125).—A continuation of previous papers (this vol., ii, 34) giving a critical revision of Stas' determinations. The present paper deals with the analysis of potassium chlorate by conversion into potassium chloride by (1) ignition, and (2) treatment with hydrochloric acid. The apparent atomic weights arrived at for the three elements concerned are as follows, the two figures given in each case being for the dry and wet method of examination respectively: Potassium, 39·0018 and 39·0028; oxygen, 15·9914 and 15·9871; chlorine, 35·5018 and 35·5028. T. A. H.

Graphic Representation of the Results of van't Hoff's Researches on "the Formation of Oceanic Salt Deposits." H. E. BOEKE (*Zeitsch. Kryst. Min.*, 1910, **47**, 273—283).—In a series of two-dimensional diagrams is expressed the conditions necessary for the crystallisation of the various double salts from aqueous solutions containing the components Na, K, Mg, Ca, SO_4, Cl. L. J. S.

Separation and Purification of Dithionates Produced in the Decomposition of Silver Sulphite or its Double Salts. HENRI BAUBIGNY (*Compt. rend.*, 1910, **150**, 466—467).—Details are given for the preparation of pure potassium dithionate from the products obtained by boiling potassium silver sulphite with water. Sodium dithionate is prepared by boiling for half an hour an aqueous solution of silver nitrate (9 grams) with sodium sulphite (20 grams). The clear liquid is treated with barium nitrate, followed by slight excess of sodium carbonate; after filtration, it is neutralised exactly with nitric acid and evaporated to crystallisation. The product is purified from sodium nitrate by taking advantage of the greater solubility of the latter in 50% alcohol. W. O. W.

The Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation. ERNST H. RIESENFELD (*Ber.*, 1910, **43**, 566—568).—A solution of potassium percarbonate ($K_2C_2O_6$) con-

taining sodium carbonate (1 mol. percarbonate: 2 mol. carbonate) liberates much more iodine from potassium iodide than does a solution containing sodium carbonate with hydrogen peroxide of crystallisation (1 mol.) and sodium hydrogen carbonate (2 mols.), although the former solution is more strongly alkaline than the latter.

This refutes Tanatar's criticisms (this vol., ii, 203) of the author's method (this vol., ii, 35) for differentiating between real percarbonates and carbonates containing hydrogen peroxide of crystallisation.

T. S. P.

Percarbonates. RICHARD WOLFFENSTEIN (*Ber.*, 1910, **43**, 639—641).—Polemical against Riesenfeld and Reinhold (this vol., ii, 33), pointing out that twelve years ago Hansen obtained a potassium percarbonate which was 99% pure (Abstr., 1898, ii, 23). It is also maintained that the products resulting from the action of carbon dioxide on sodium dioxide and sodium trioxide, namely, sodium dioxycarbonate and sodium trioxycarbonate (Abstr., 1908, ii, 180, 183), are definite chemical compounds. T. S. P.

Sodium Hyposulphite. MAX BAZLEN and AUGUST BERNTHSEN (*Ber.*, 1910, **43**, 501—504).—Polemical against Orloff, who, in a book on formaldehyde, deals with hyposulphurous acid, the hyposulphites, formaldehydesulphoxylate, etc., and claims to show that the views of Schützenberger and Grossmann with respect to the constitution of the hyposulphites are correct. The conclusions which Orloff draws from his own experiments are untrustworthy, since he did not take precautions to prevent oxidation of the solutions of the hyposulphite used. T. S. P.

Hydrolysis of Ammonium Salts of Volatile Acids. KURT BUCH (*Zeitsch. physikal. Chem.*, 1910, **70**, 66—87).—The paper deals with the degree of hydrolysis in solutions of ammonium carbonate and carbamate and of ammonium phenoxide at 25°. The method of measurement employed was to determine the partial pressure of one or more of the components by passing a current of indifferent gas (electrolytic gas) through the solution, the substances carried over being absorbed in suitable reagents.

In the case of the ammonium carbonate-carbamate mixture, the partial pressures both of ammonia and carbon dioxide were determined; the former gas was absorbed in hydrochloric acid, and the latter in barium hydroxide solution. From the results, the free and bound ammonia and carbon dioxide concentrations and the carbamate and hydrogen carbonate concentrations in the different solutions have been calculated. The hydrolysis and equilibrium constants are then calculated from the above data, and the known equilibrium constants concerned by application of the law of mass action, with the following results: Hydrolysis constant of the hydrogen carbonate,

$$K_1 = [p_{NH_3} \times p_{CO_2}]/([NH_4^{\cdot}] \times [HCO_3']) = 37—69;$$

hydrolysis constant of the carbamate,

$$K_2 = (p_{NH_3} \times p_{CO_2})/([NH_4^{\cdot}][NH_2CO_2']) = 39—84 \times 10^3;$$

equilibrium constant carbonate/carbamate,

$$K_3 = [NH_3][HCO_3']/[NH_2CO_2'] = 0{\cdot}42—1{\cdot}68.$$

The above constants are calculated on the assumption of complete dissociation of the salt, which is not strictly justified in the relatively high concentrations used.

The value of K_3 is also calculated from Fenton's observations on the carbonate/carbamate equilibrium at 20—22° (compare Abstr., 1886, 501). For seven solutions the "constant" only varies between 0·52 and 0·97, in fair agreement with the above results.

The hydrolysis constant K_1 for the hydrogen carbonate has also been calculated from the known dissociation constants of the components, and the value is about eight times greater than the observed. No satisfactory explanation of this discrepancy has been found.

Most of the data for the hydrolytic dissociation of ammonium phenoxide have already been published (compare Abstr., 1908, i, 259). The hydrolysis of this salt can also be calculated in an approximate way from the increase in the solubility of phenol in water due to ammonia, and the experimental results are in fair agreement with the theory. G. S.

Reaction between Ammonium Chloride and Potassium Dichromate when Heated. GEORGE B. FRANKFORTER, V. H. ROEHRICH, and E. V. MANUEL (*J. Amer. Chem. Soc.*, 1910, 32, 178—184).—The method of preparing nitrogen by heating a mixture of potassium dichromate and ammonium chloride is usually supposed to involve the following reaction: $2NH_4Cl + K_2Cr_2O_7 = Cr_2O_3 + 2KCl + 4H_2O + N_2$. The authors have observed that the gas thus obtained contains, in addition to nitrogen, considerable quantities of nitric oxide and nitrogen peroxide, and that this equation, therefore, cannot be correct. The reaction has been studied, and the following results obtained.

The reaction which takes place when the mixture is heated at 290° is different from that which occurs at a dull red heat, the composition of the gas evolved and of the residue left after lixiviation being different in the two cases. A mixture of ammonium chloride and potassium dichromate does not undergo any change until a temperature of 210° is attained. The mixture then becomes yellowish-brown, owing to the formation of chromium dioxide. At 260°, a slate-coloured residue is obtained, which, on lixiviation with water, leaves small, greenish-black, iridescent spangles of a hydrated chromium oxide, $Cr_2O_3,2H_2O$. The change which takes place does not depend only on the temperature, but also on the proportions of the salts employed. At 370°, in presence of a considerable excess of ammonium chloride, chromium chloride and ammonia are formed. If, however, the potassium dichromate is in large excess, a black residue is obtained, together with some unchanged dichromate. Under certain conditions, chlorine is liberated, and in some cases, a nitride of chromium is produced. It is suggested that the complexity of the reaction is largely due to the dissociation of ammonium chloride, which is the first change to take place when the mixture is heated. E. G.

Atomic Weights of Silver, Lithium, and Chlorine. THEODORE W. RICHARDS and HOBART HURD WILLARD (*J. Amer. Chem. Soc.*, 1910, 32, 4—49 *)—It is pointed out that the present uncertainty

* and *Zeitsch. anorg. Chem.*, 1910, 66, 229—287.

with regard to the atomic weight of silver is very unsatisfactory, since most other elements are referred to oxygen through silver, and their atomic weights cannot be known accurately until the relation between silver and oxygen is definitely established. A review is given of the work that has already been done with a view to the determination of the oxygen-silver ratio.

The present paper gives an account of further work on this subject. A careful study has been of made of the three ratios: $LiCl : AgCl$, $LiCl : Ag$, and $LiCl : LiClO_4$, and by means of the last two the ratio $4O : Ag$ has been calculated thus: $4O/LiCl : LiCl/Ag = 4O/Ag$. The methods employed to purify the materials and the numerous precautions observed to ensure accuracy are described in detail.

The ratios $LiCl : AgCl$ and $LiCl : Ag$ were first determined. Pure lithium chloride was obtained by the following method. The lithium was precipitated as fluoride, and this salt was converted into the nitrate or perchlorate, which was repeatedly recrystallised. The perchlorate was decomposed by heat, whilst the nitrate was treated with ammonium carbonate, and the precipitated lithium carbonate converted into the chloride. The average of seven determinations of the amount of silver chloride precipitated by a weighed quantity of lithium chloride gave the ratio $LiCl : AgCl = 0{\cdot}295786$, corresponding with 6·940 as the value of the atomic weight of lithium [Ag = 107·880]. In another series of seven experiments, in which the amount of silver required for complete precipitation with a weighed quantity of lithium chloride was determined, the average result gave the ratio $LiCl : Ag = 0{\cdot}392992$, corresponding with 6·939 for the atomic weight [Ag = 107·880].

The ratio $LiCl : LiClO_4$ was determined by converting the former salt into the latter. This was effected by dissolving a weighed quantity of lithium chloride in a slight excess of perchloric acid and removing the hydrochloric acid and the excess of perchloric acid by passing a current of air through the flask containing the mixture, the temperature being so regulated that ebullition did not take place. The perchlorate was afterwards fused, dried at 300°, and weighed. The gain in weight being due to oxygen alone gave at once the ratio $4O : LiCl$. From the known ratio $LiCl : Ag$, the atomic weight of silver was calculated. The average result of six experiments gave the ratio $4O : Ag = 0{\cdot}593301$, whence the atomic weight of silver is 107·871 [O = 16·000]. With this value for the atomic weight of silver, the atomic weight of lithium becomes 6·939, and that of chlorine, 35·454.

E. G.

Solubility of Silver Chloride, Barium Sulphate, and Calcium Sulphate at High Temperatures. ARTHUR C. MELCHER (*J. Amer. Chem. Soc.*, 1910, **32**, 50—66).—The conductivity of saturated solutions of silver chloride and barium sulphate at 18°, 50°, and 100°, and of calcium sulphate at 18°, 50°, 156°, and 218°, has been determined by means of the platinum-lined steel bomb described by Noyes and Coolidge (Abstr., 1904, ii, 226). From the values of the conductivities, the solubilities have been calculated with the following results, expressed in milli-equivalents per litre: Silver chloride, 0·0105 at 18°; 0·0365 at 50°; 0·0147 at 100°. Barium sulphate, 0·0190 at 18°;

0·0212 at 25°; 0·0288 at 50°; 0·0334 at 100°. The values found at 18° are compared with those obtained by Böttger (Abstr., 1906, ii, 656) and Kohlrausch (Abstr., 1908, ii, 814). From these data, the heats of solution of silver chloride and barium sulphate have been calculated, and found to agree fairly well with those recorded by Thomsen.

In the case of calcium sulphate, the solubilities (in milli-equivalents per litre) have been found to be as follows: Gypsum, 29·5 at 18°; 30·0 at 50°; 23·3 at 100°. Soluble anhydrite, 22·8 at 100°, and 6·4 at 156°. Anhydrite, 9·2 at 100°, 2·7 at 156°, and 0·7 at 218°. These results are compared with those of previous observers. The solubility relations of these three forms of calcium sulphate are represented by means of curves. The transition temperature for the metastable system (gypsum, soluble anhydrite, solution) was found to be about 97°.

The equivalent concentrations of the ions in saturated calcium sulphate solutions have been calculated, and the results are tabulated. It is shown that the ionisation in a solution, saturated with gypsum at 100°, is 39%, and that in a solution, saturated with anhydrite at 156°, it is 45%. The ionisation relations of calcium sulphate are compared with those of magnesium sulphate which were studied by Noyes and Melcher (Abstr., 1908, ii, 347). The degree of ionisation of calcium sulphate is almost identical with that of magnesium sulphate at 18°, but is slightly less at 100° and 156°. E. G.

Solubility of Slightly Soluble Calcium Salts in Aqueous Solutions of Ammonium Salts, Especially of Triammonium Citrate. ARTHUR RINDELL (*Zeitsch. physikal. Chem.*, 1910, **70**, 452—458. Compare Spiller, Trans., 1857, **10**, 110).—The nature of the changes occurring when calcium carbonate is dissolved in solutions containing certain ammonium salts in varying concentrations has been investigated by physico-chemical methods.

The solubilities in millimols. per litre at 25° of calcium carbonate in solutions containing 500 millimols. of the ammonium salts per litre are as follows: Ammonium chloride, 5·008; ammonium nitrate, 5·267; triammonium citrate, 66·87. It is probable that the first two values are due to the usual increased solubility of slightly soluble salts in solutions not containing common ions, but the much greater solubility in solutions of ammonium citrate indicates the formation of complex anions containing calcium. This conclusion has been confirmed by cryoscopic and transport measurements.

The presence of ammonium salts, more particularly the citrate, thus renders incomplete the precipitation of calcium, even as oxalate, a result important for gravimetric determinations. G. S.

Red Lead. III. JAROSLAV MILBAUER (*Chem. Zeit.*, 1910, **34**, 138—140. Compare Abstr., 1909, ii, 889).—Experiments above the optimum temperature for the formation of red lead show that the decomposition in a vacuum is complete at 530°, the temperature being higher when oxygen, air, or carbon dioxide is present—about 600° for oxygen.

The curve of decomposition of lead peroxide has breaks indicating the formation of the oxides: Pb_2O_3, Pb_3O_4, and PbO. C. H. D.

Liquid-Crystalline Phases of the Monohalides of Thallium and Silver. H. STOLTZENBERG and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1910, **71**, 641—648).—It has been known for a long time that silver iodide exists in a liquid-crystalline form, and the authors now show by microscopic observations that the same is true for the chloride and bromide of silver and the three halides of thallium. The proof of this statement was obtained by observations of the fused salts as they solidified, and also by noticing that small dust particles which were in motion in the amorphous fused mass continued their movements in the liquid-crystalline phase.

In the case of the chloride and bromide of thallium and of silver bromide, the solid phase formed on cooling is succeeded by a second solid regular phase. The regular phases of the chlorides and bromides of thallium and silver become anisotropic on cooling to room temperature, and there is some evidence that the two iodides can also exist in anisotropic forms at low temperatures.

The phenomena observed as the individual salts solidify are described in detail. The melting points of the salts are as follows: Thallium chloride, 407°; the bromide, 441°; the iodide, 422°; silver iodide, about 500°. G. S.

Mercury Haloids. J. S. VAN NEST (*Zeitsch. Kryst. Min.*, 1910, **47**, 263—272).—Mixed crystals of mercuric chloride (D 5·451; $a:b:c=0·7251:1:1·0697$) with mercuric bromide (D 6·064; $a:b:c=0·6826:1:1·7953$) are all orthorhombic, but of three kinds, differing in habit, cleavage, and optical orientation. Those containing from 100% to $43\frac{1}{2}$% $HgCl_2$ are isomorphous with the pure chloride, and have a prismatic habit parallel to the prism $m\{110\}$; $a:b:c$ varies from the value given above for the pure chloride to $0·7067:1:1·0464$. There is then a gap in the series. Crystals containing from 29% to 24% $HgCl_2$ are prismatic in the direction of the brachydome $u\{012\}$; these are probably to be considered as belonging to the double salt,

$$HgCl_2,2HgBr_2\ (a:b:c=0·6284:1:1·0242),$$

with isomorphous mixing of chloride and bromide. After another gap in the series, the mixed crystals containing from 10% to 0% $HgCl_2$ (that is, to the pure bromide) are tabular parallel to $c\{001\}$, with $a:b:c$ varying from $0·6909:1:-$ to the value for the pure bromide.

Mixed crystals of mercuric bromide with yellow mercuric iodide (D 6·282; $a:b:c=0·6269:1:1·7893$) form an unbroken series of orthorhombic crystals from 100% to 3% $HgBr_2$. With less bromide the crystals are isomorphous with the red, tetragonal mercuric iodide (D 6·294; $a:c=1:2·008$). Mercuric chloride is thus dimorphous, and mercuric bromide trimorphous, in these mixed crystals.

The oxychloride $HgCl_2,2HgO$ is monoclinic, with

$$a:b:c=1·9782:1:1·0452;\ \beta=125°57',$$

and appears to be distinct from the monoclinic oxychloride of the same composition measured by Blaas in 1879. Crystalline scales of the oxychlorides $HgCl_2,3HgO$ and $HgCl_2,4HgO$ were also prepared. L. J. S.

Dimercurammonium Bromides. H. GAUDECHON (*Compt. rend.*, 1910, **150**, 467—470. Compare Abstr., 1909, ii, 670).—The reaction $2HgBr_2 + 4NH_3 = NHg_2Br,xNH_4Br + (3 - x)NH_4Br$ has been studied by allowing the system $2HgBr_2 + 4NH_3$ to remain with water in different proportions at 8—10° until equilibrium was obtained, and then determining the composition of the precipitate and the residual solution. The results are given in the form of a table, from which it appears that three solid phases exist, corresponding with the compounds: $4NHg_2Br,HgBr_2$; NHg_2Br,NH_4Br, and $NHg_2Br,3NH_4Br$.

W. O. W.

Action of Thionyl and Sulphuryl Chlorides on Mercury and Mercuric Oxide. H. B. NORTH (*J. Amer. Chem. Soc.*, 1910, **32**, 184—187).—It has been stated by Spelta (Abstr., 1904, ii, 479) that sulphuryl chloride does not react with red mercuric oxide even on prolonged heating, but that with yellow mercuric oxide the reaction takes place according to one of the following equations: $2HgO + SO_2Cl_2 = HgSO_4 + HgCl_2$ and $HgO + SO_2Cl_2 = HgCl_2 + SO_3$. The present author has repeated this work, and has also studied the action of sulphuryl chloride on mercury and of thionyl chloride on mercuric oxide and mercury.

Yellow mercuric oxide reacts slowly with sulphuryl chloride at the ordinary temperature, with formation of a mixture of mercurous and mercuric chlorides. If the yellow oxide is heated with an excess of the reagent at 150° in a sealed tube, mercuric chloride and sulphur trioxide are formed, with not more than mere traces of sulphate. The red oxide was found to behave similarly at 160—180°.

Sulphuryl chloride reacts with mercury at 160—180° in accordance with the equation: $Hg + SO_2Cl_2 = HgCl_2 + SO_2$. When an excess of mercury is used, the solid product consists entirely of mercurous chloride.

When thionyl chloride is heated with mercuric oxide at 160° in a sealed tube, mercuric chloride, sulphuryl chloride, and sulphur monochloride are formed, thus: $HgO + 5SOCl_2 = HgCl_2 + 3SO_2Cl_2 + S_2Cl_2$. If the thionyl chloride is not present in large excess, the reaction probably proceeds according to the equation: $HgO + SOCl_2 = HgCl_2 + SO_2$.

If thionyl chloride is heated with mercury at 150° in a sealed tube, a reaction takes place in accordance with one of the following equations, depending on the proportions of the reagents used: $Hg + 4SOCl_2 = HgCl_2 + 2SO_2Cl_2 + S_2Cl_2$; $3Hg + 4SOCl_2 = 3HgCl_2 + 2SO_2 + S_2Cl_2$.

E. G.

Specific Heat of Pure Yttrium Oxide. SEBASTIAN M. TANATAR and I. VOLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 96—102).—In order to determine the valency of yttrium, the authors have measured the specific heat of carefully purified yttrium oxide.

Commercial "pure yttrium oxide" contains an appreciable proportion of erbium oxide, from which it was freed by means of the sulphate and propionate, the latter crystallising well from water. The purity of the oxide obtained in this way was established by analysis of the fumarate and propionate. The pure oxide, which was obtained as a white

powder, has $D^{16.5-18}$ 5·326—5·380; Cleve gave 5·028, Nilson and Pettersson (Abstr., 1880, 838) 5·046, and Muthmann and Böhm (Abstr., 1900, ii, 209) 4·842. Determination of the specific heat of the oxide by Berthelot's method (compare Tanatar, Abstr., 1907, ii, 261) over a temperature interval of 80° gave the mean value 0·11729, the molecular heat being 26·507; the corresponding values given by Nilson and Pettersson (*loc. cit.*) were 0·1026 and 23·1876. The atomic heat of oxygen in the oxides, R_2O_3, of arsenic, bismuth, chromium, iron, antimony, boron, and aluminium varies roughly between 4 and 5; taking the number 4·5, the value 26·507 for the molecular heat of the oxide gives 6·503 for the atomic heat of yttrium, and thus confirms the tervalency of the metal. T. H. P.

Alumina from the Oxidation of Aluminium Amalgam in Air. P. ROGER JOURDAIN (*Compt. rend.*, 1910, **150**, 391—394. Compare Zunino, Abstr., 1900, ii, 348).—The aluminium oxide produced by the spontaneous oxidation of aluminium amalgam contains 46·5% of water, but does not appear to be a definite pentahydrate, as stated by Zunino. It is capable of absorbing more water when exposed to moist air, and when placed in a dry atmosphere, or if heated to 200° in a vacuum, water is slowly lost, but the weight does not become constant even after several days. The calcined oxide is very hygroscopic. W. O. W.

The Manganate Fusion. PAUL ASKENASY and S. KLONOWSKI (*Zeitsch. Elektrochem.*, 1910, **16**, 104—114).—The oxidation of the lower oxides of manganese to potassium manganate by heating them with potassium hydroxide in an atmosphere containing oxygen is investigated.

The dissociation pressure of manganese dioxide (artificially prepared) is found to be: at 382°, 23 mm.; at 448°, 125 mm.; at 478°, 200 mm., and at 536° more than 1040 mm. The purest potassium manganate which could be prepared contained a small excess of potassium hydroxide, and its dissociation pressure was found to be, at 410°, 2 mm.; at 454°, 5 mm.; at 548°, 40 mm.; at 586°, 109 mm.; at 616°, 235·5 mm.; at 652°, 568 mm.; and at 668°, 763 mm.

In the fusion experiments the potassium hydroxide was usually added to the powdered manganese oxide in the form of a strong solution, the mixture being then dried and powdered. Drying the air or oxygen improves the yields slightly. The results obtained, starting with manganese dioxide or manganic oxide, Mn_2O_3, are almost identical. In both cases the quantity of manganate formed increases as the temperature rises up to the point at which the pressure of the oxygen is equal to the dissociation pressure of the manganate; at higher temperatures the manganate is, of course, decomposed. In air the best temperature is about 600°; in oxygen it is near 700°. Using an excess of manganese oxide, some 60 to 65% of the potassium hydroxide employed is converted into manganate under the best conditions. Prolonging the time of heating beyond one hour does not increase the yield materially. The absorption of oxygen takes place at 240°, but more slowly than at higher temperatures. T. E.

Alkali Mangani-manganates. VICTOR AUGER (*Compt. rend.*, 1910, **150**, 470—472. Compare Abstr., 1904, ii, 262; Sackur, this vol., ii, 214, 215).—The author confirms the existence of Sackur's salts, $5K_2O,Mn_5O_{13}$ and $2Na_2O,Mn_2O_5$, and in the case of the sodium salt has succeeded in isolating the substance, but not in a state of purity. This was accomplished by heating in a silver crucible 10 grams of potassium permanganate with 100 grams of sodium hydroxide and 20 c.c. of water. The crystalline mass was washed with a concentrated solution of sodium hydroxide, when the compound was obtained as a micro-crystalline, bluish-green powder, which underwent immediate decomposition on treatment with water.

W. O. W.

The Equilibrium Diagram of Iron-Carbon Alloys. E. HEYN (*Zeitsch. Elektrochem.*, 1910, **16**, 102—104).—Polemical. A reply to Wüst (Abstr., 1909, ii, 1017).

T. E.

The Decarburisation of Iron by Gaseous Oxidising Agents. HANS BECKER (*Metallurgie*, 1910, **7**, 41—59).—The behaviour of iron containing carbon in contact with mixtures of carbon monoxide and dioxide has been studied. The extent to which white cast-iron, or iron containing temper-carbon, is decarburised increases with the percentage of carbon dioxide and with the temperature. A mixture of gases which is without action on the carbon content of tempered cast-iron contains 30% CO_2 at 800°, 12% at 900°, and 2·85% at 1000°. The action on white iron at 800° is less, whilst at 800° and 1000° no difference can be observed between the behaviour of the two kinds of iron. This is considered to favour Wüst's view (Abstr., 1908, ii, 286), that in the production of malleable cast-iron the carbon is always converted into temper-carbon before being oxidised.

Oxidation of the iron does not take place if the mixture contains 28% of carbon dioxide at 900° or 24% at 1000°, and such mixtures are therefore suitable for decarburisation.

C. H. D.

The Influence of Antimony and Tin on the Iron-Carbon System. PAUL GOERENS and K. ELLINGEN (*Metallurgie*, 1910, **7**, 72—79).—Antimony and tin modify the equilibrium of iron and carbon in the same way as phosphorus (Goerens, Abstr., 1909, ii, 892), forming a compound with the iron, and giving rise to a ternary eutectic. Antimony greatly lowers the solubility of carbon in iron, whilst tin has less effect.

In an alloy containing 3·5% C, antimony lowers the initial freezing point of the austenite, and also the eutectic temperature, until the latter coincide at 1090° and 5% Sb. The ternary eutectic, composed of austenite, cementite, and the antimonide, Fe_2Sb_3, solidifies at 950°. In an alloy containing 3% C, the austenite curve meets that of the binary eutectic at 1070° and about 14% Sb. The freezing-point surface is thus made up of three surfaces, corresponding with the separation of austenite (containing some antimony in solid solution), cementite, and antimonide. The formation of pearlite at 690° is unaffected by the presence of antimony. Microscopical

examination confirms these results. The antimonide is less readily coloured on heat-tinting than cementite. The antimony may be estimated by precipitating as sulphide, dissolving in hot hydrochloric acid, and titrating with $N/1$-potassium bromate, with indigotin as indicator.

The ingots obtained when tin is added are often not homogeneous, owing to the formation of two liquid layers. The system resembles that in which antimony is present, the eutectic point being near 950°. The pearlite point is practically unaltered. The composition of the stannide is unknown. C. H. D.

Positive Ferric Hydroxide. HERMANN W. FISCHER (*Zeitsch. anorg. Chem.*, 1910, **66**, 37—52. Compare Malfitano, Abstr., 1909, ii, 473).—A study of the dehydration curves of natural and artificial colloidal ferric hydroxides shows that limonite is identical with the yellow colloid, whilst hæmatite is identical with the glistening, blackish-red product obtained when ferric chloride solution is heated in a sealed tube. Xanthosiderite and hydrolimonite are merely colloids containing variable quantities of water. Goethite is a definite, crystalline hydroxide. The yellow colloid, or natural limonite, shows a rapid increase in the rate of dehydration when the water-content has sunk to 1 mol., the colour changing to red.
C. H. D.

Cobalt–Gold Alloys. WALTER WAHL (*Zeitsch. anorg. Chem.*, 1910, **66**, 60—72).—Pure gold and powdered cobalt may be fused in nitrogen in porcelain tubes. The cobalt at first attacks the porcelain, but the oxide present being thus removed, subsequent fusions do not cause any further attack. Pure cobalt is readily undercooled, a quantity of 20 grams being cooled as much as 216° below its freezing point, solidification then taking place suddenly. The same behaviour is observed in the alloys.

The freezing-point curve consists of two branches, meeting at a eutectic point at 997° and 72·9 atomic % of gold (90% Au). The saturated solid solutions contain 3·5% and 94% Au respectively. The microscopic structure is in accordance with these conclusions.

The whole of the alloys are magnetic. The magnetisability falls with increasing gold-content, rapidly at first, and then more slowly. It increases with the temperature, being three times as great at the eutectic temperature as in the cold.

The crystals rich in cobalt must be regular above 1140°, being isomorphous with β-cobalt, but assume hexagonal forms in the α-condition. C. H. D.

Readily Soluble Polychromates of the Heavy Metals. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1910, **66**, 7—19).—The soluble dichromates of the heavy metals can only be crystallised by slow evaporation of their solutions in a vacuum (Schulze, Abstr., 1896, ii, 24). For the present investigation, the carbonates were prepared by dropping a solution of the metallic chloride into a cold solution of ammonium carbonate saturated with carbon dioxide. The precipitate was left in contact with the solution until no further microscopic change occurred, and was then washed with cold water and dried.

The dichromates were prepared by dissolving the carbonates in 2*N*-chromic acid.

Zinc dichromate, $ZnCr_2O_7,3H_2O$, forms transparent, orange crystals. Evaporation of the mother liquor yields an insoluble basic salt, the solution then containing a more soluble salt, which is obtained from an acid solution in transparent, dark red, deliquescent crystals of *zinc trichromate*, $ZnCr_3O_{10},3H_2O$.

Cadmium dichromate, $CdCr_2O_7,H_2O$, behaves similarly, the solutions decomposing on evaporation into an insoluble orange powder and *cadmium trichromate*, $CdCr_3O_{10},H_2O$, which forms dark red, deliquescent, crystalline crusts.

Cupric dichromate, $CuCr_2O_7,2H_2O$, also decomposes when its solution is evaporated, but the trichromate further decomposes on evaporation into the dichromate and *cupric tetrachromate*, $CuCr_4O_{13},2H_2O$, which forms small, deliquescent crystals, decomposed by water.

Solutions of nickel dichromate do not crystallise well, and the trichromate has only been obtained in an amorphous condition. Cobalt dichromate, $CoCr_2O_7,H_2O$, is semi-crystalline, and solutions which should yield the trichromate deposit greyish-black crusts, which may contain a dichromate of tervalent cobalt, formed according to the equation: $2CoCr_2O_7 = Co_2(CrO_4)_3 + CrO_2$ in the presence of an excess of chromic acid.

It has not been found possible to prepare a homogeneous mânganous dichromate, the chromic acid oxidising a part of the manganese to manganese dioxide. C. H. D.

Molybdenum Dichloride. ARTHUR ROSENHEIM and FRANZ KOHN (*Zeitsch. anorg. Chem.*, 1910, **66**, 1—6).—A molybdenum dichloride was described by Blomstrand (*J. pr. Chem.*, [i], 1857, **71**, 449; 1859, **77**, 88; 1861, **82**, 433), and was found to exhibit abnormal properties. By heating aluminothermic molybdenum in chlorine, a yellow product is obtained, which always contains other chlorides. Recrystallisation from concentrated hydrochloric acid gives yellow needles. Blomstrand's formula, $Mo_3Cl_6,6H_2O$, is not confirmed, the analyses corresponding with the formula: $Mo_3Cl_6,HCl,4H_2O$. The crystals lose hydrogen chloride in air, becoming green, but become yellow again in an atmosphere of hydrogen chloride. The reaction with an ammoniacal silver solution proves the molybdenum to be bivalent. Heating at 100° or 130° in hydrogen chloride yields a yellow residue of Mo_3Cl_6,H_2O.

Water at first removes only one chlorine atom from the compound $Mo_3Cl_6,HCl,4H_2O$, but when it is dissolved in potassium hydroxide and precipitated with acetic acid, the precipitate has the composition $Mo_3Cl_4(OH)_2$. Blomstrand's formula for the compound with ammonium chloride, $(NH_4)_2Mo_3Cl_8,2H_2O$, could not be confirmed, the analytical results not corresponding with any simple formula. The pyridinium salt has the composition: $3C_5NH_5,H_3Mo_3Cl_9,3H_2O$. C. H. D.

Two New Complex Acids. ARTURO MIOLATI (*Zeitsch. physikal. Chem.*, 1910, **70**, 330—334. Compare Abstr., 1908, ii, 595).—One of the acids in question was prepared by boiling potassium tellurate

and potassium molybdate, and gradually adding sufficient nitric acid to render the solution moderately acid; on cooling the filtered solution, lustrous crystals are obtained, which are purified by recrystallisation from water acidified with hydrochloric acid. The same product is obtained by starting with telluric acid and yellow molybdic acid; in this case, it is necessary to add potassium hydroxide and nitrate to prevent the solution from becoming too strongly acid. It has the composition $Te_2O_{11}K_{10},12MoO_3,18H_2O$, or, possibly,

$$TeO_6HK_5,6MoO_3,8H_2O;$$

its constitution has not yet been established.

When formic acid is added to ammonium molybdate and the solution warmed, slender, colourless, granular crystals separate; an exactly similar result is obtained when potassium molybdate is used. The composition of these salts corresponds with the formulæ: $OH\cdot CH(Mo_2O_7NH_4)_2,2H_2O$ and $OH\cdot CH(Mo_2O_7K)_2,H_2O$; they cannot by recrystallised from hot water without decomposition. The investigation is being continued. G. S.

Arsenosomolybdates. FRITZ EPHRAIM and HERMANN FEIDEL (*Zeitsch. anorg. Chem.*, 1910, **66**, 53—59).—A solution of 3 mols. of potassium carbonate, 6 mols. of molybdenum trioxide, and 1 mol. of arsenious oxide deposits crystals of potassium molybdate, and then a white mass, which crystallises from water, and is the *salt*,

$$3K_2O,As_2O_3,5MoO_3,3H_2O.$$

A second *salt*, $3K_2O,As_2O_3,8MoO_3,18H_2O$, forms white crystals; D^{16} 3·15. A *sodium* salt, $Na_2O,As_2O_3,2MoO_3,6H_2O$, forms large, rectangular crystals; D^{16} 3·43. The *salt*, $2Na_2O,As_2O_3,4MoO_3,13H_2O$, has also been obtained. Crystalline ammonium salts could not be prepared, but an *ammonium barium* salt, probably

$$3(NH_4)_2O,2BaO,5As_2O_3,10MoO,50H_2O,$$

D^{16} 3·14, has been prepared. Two *ammonium cupric* salts,

$$(NH_4)_2O,CuO,2As_2O_3,4MoO_3,2H_2O,$$

octahedral crystals, D^{16} 2·50, and $2(NH_4)_2O,CuO,3As_2O_3,6MoO_3,13H_2O$, short, hexagonal prisms, D^{16} 3·17, have been obtained. C. H. D.

Dissimilarity in Properties of Dextro- and Lævo-rotatory Forms of Potassium Silicotungstate, and, in general, of Optically Active Crystals. HIPPOLYTE COPAUX (*Compt. rend.*, 1910, **150**, 475—477).—Wyrouboff has shown that aqueous solutions of Marignac's salt, $4K_2O,24WO_3,2SiO_2,36H_2O$, deposit dextrorotatory crystals (Abstr., 1897, ii, 173). Lævorotatory crystals, however, are occasionally formed, and when a fresh solution is inoculated with one of these, only the lævo-form is deposited. A solution of the lævorotatory crystals, however, only yields the dextrorotatory crystals, unless inoculated. Both forms occur in highly refractive, hexagonal prisms terminated by hexagonal pyramids, and there appears to be no crystallographic differences between them. The two modifications have almost the same solubility, but the dextrorotatory variety crystallises more rapidly and undergoes dissolution more slowly than the lævorotatory modification. Similar phenomena have been observed, although in a less marked degree, with potassium metatungstate, borotungstate, silicomolybdate, and chlorate. W. O. W.

Metallic Titanium. LUDWIG WEISS and HANS KAISER (*Zeitsch. anorg. Chem.*, 1910, **65**, 345—402).—Potassium titanifluoride is most conveniently prepared by fusing rutile with potassium hydrogen fluoride, and crystallising the product from water containing a little hydrofluoric acid. It does not contain water of crystallisation. Reduction with sodium yields an amorphous product containing 68—76% Ti, or 86% after a repetition of the reduction. If massive aluminium is added to fused potassium titanifluoride, a vigorous reaction occurs, and a crystalline product having the formula Al_3Ti_2 is obtained.

Titanium is only very incompletely oxidised by heating in air. For analysis, the titanium is heated in air, fused with potassium hydrogen sulphate, dissolved in sulphuric acid, neutralised with ammonia, and boiled. The precipitate is ignited, and weighed as titanium dioxide. If aluminium is present, the ammonia precipitate is warmed with acetic acid, which dissolves the aluminium, or the ignited precipitate is fused with sodium carbonate and borax and extracted with water, only the titanium remaining insoluble. Titanium may be estimated volumetrically by Newton's method (Abstr., 1908, ii, 325), or colorimetrically with hydrogen peroxide.

After compressing into rods and heating electrically in a hydrogen or nitrogen vacuum, the compact product contains 97·5% Ti, and melts at 2200—2400°. It is not possible to remove the whole of the aluminium, if present, by volatilisation. The metal is completely converted into nitride by heating in nitrogen. Titanium has D^{19-20} 5·174; specific heat, 0·1418; heat of combustion, 24·443 cal. per equivalent.

C. H. D.

Titanium. MATTHEW A. HUNTER (*J. Amer. Chem. Soc.*, 1910, **32**, 330—336).—It is shown that pure titanium cannot be obtained either by the methods of Berzelius (*Ann. Phys. Chem.*, 1825, [ii], **4**, 3) and Wöhler and Deville (*Compt. rend.*, 1857, **45**, 480), which consist in the reduction of the titanifluorides with alkali metals, or by Moissan's method (Abstr., 1895, ii, 272) of reducing the dioxide by means of carbon. By a modification of Nilson and Pettersson's method (Abstr., 1887, 778), however, in which titanium tetrachloride is reduced with sodium in an air-tight steel cylinder, a yield of pure metal has been obtained amounting to 90% of the theoretical.

Titanium resembles polished steel in appearance. It is hard and brittle when cold, but is remarkably malleable at a low red heat. The metal has D 4·50, and m. p. between 1800° and 1850°. E. G.

Zirconium. EDGAR WEDEKIND and S. JUDD LEWIS (*Annalen*, 1910, **371**, 367—387. Compare Trans., 1909, **95**, 456).—An investigation of the chemical and physical properties of several specimens of zirconium of various degrees of purity, analyses of many of which have been recorded previously (*loc. cit.*). The pure metal has not yet been obtained, but a sample has been prepared by a method to be described later, which contains 97% of the element.

The following physical properties of the pure metal have been deduced from the results obtained with the various specimens: m. p. 2330—2380°; D 6·39; specific heat, 0·0683—0·0735; hardness,

6·5—7·0; the fused metal has roughly the same electrical conductivity as brass, and becomes coated with a film of oxide when used as the anode, with platinum as a cathode, in the electrolysis of dilute hydrochloric acid; it falls between platinum and silver in the electrical tension series, the first members of which run in the order: Au, Pt, Pd, Ta, Zr, Ag, Hg, Cu, etc.

Metallic zirconium is not attacked by water, neither is it acted on by the air; when heated in air at 100—200°, it slowly absorbs nitrogen, which becomes displaced subsequently by oxygen. It absorbs hydrogen at a red heat, and combines with chlorine, bromine, iodine, sulphur, and phosphorus at a moderate temperature; when acted on by ammonia at a dull-red heat, it yields a greyish-green powder, which evolves ammonia when heated in a Bunsen flame, but not when treated with water. Unlike titanium and silicon, zirconium does not readily alloy with iron; a *ferrozirconium* containing 1% of zirconium was obtained by heating the components together in a vacuum.

Zirconium is dissolved quite readily by dilute solutions of hydrofluoric acid, but is not attacked by nitric acid, and only slightly by hydrochloric acid; it dissolves slowly when warmed with strong sulphuric acid, but if heated rapidly with the acid, a violent reaction ensues, which leads occasionally to an explosion; aqua regia does not act on the metal immediately.

Zirconium is not attacked by aqueous alkalis, but reacts with the fused alkali hydroxides; it reacts with explosive violence when fused with potassium nitrate, also when heated with certain oxides, such as copper oxide, lead oxide, etc. W. H. G.

Bismuth Peroxides. ALEXANDER GUTBIER and R. BÜNZ (*Sitzungsber. physikal.-med. Soz. Erlangen*, 1908, **40**, 96—104. Compare Abstr., 1907, ii, 181; 1908, ii, 701; 1909, ii, 407).—Alkaline solutions of hypochlorites react slowly with bismuth compounds, especially with the basic nitrate, yielding brown products. The velocity of oxidation increases with the alkalinity of the solution. The products are never homogeneous, but after extracting with cold concentrated nitric acid, a brown residue containing active oxygen is obtained. These products are not identical with "bismuthic acid." Potassium permanganate does not convert bismuth compounds into a peroxide. C. H. D.

Halide Bases of Tantalum. WILLIAM H. CHAPIN (*J. Amer. Chem. Soc.*, 1910, **32**, 323—330).—Van Haagen (*Diss.*, 1909), in attempting to prepare a lower bromide of tantalum by reducing the pentabromide with hydrogen, obtained a small quantity of a green compound, which is very stable and has remarkable tinctorial properties. A tantalum chloride of similar character has been obtained by Chabrié (Abstr., 1907, ii, 477) by reducing the pentachloride with sodium amalgam, and was regarded by him as the dichloride, $TaCl_2,2H_2O$.

It has now been found that by means of Chabrié's method, Van Haagen's bromide can be obtained in a yield of about 15% of the theoretical. The product thus prepared is remarkably pure, and consists of minute, black, hexagonal crystals, but the powdered substance

is dark green. Analysis has shown that the compound is not a dibromide, but has the composition $Ta_6Br_{14},7H_2O$. On treatment with silver nitrate, it is found that only two of the bromine atoms are in the ionic condition, and the compound must therefore be represented by the formula $(Ta_6Br_{12})Br_2,7H_2O$. The molecular weight has been confirmed by cryoscopic and ebullioscopic determinations. When the substance is treated with sodium hydroxide, it is converted into the *hydroxide*, $Ta_6Br_{12}(OH)_2,10H_2O$, which forms thin, hexagonal plates. On dissolving the hydroxide in hydrochloric acid or evaporating a solution of the bromide with hydrochloric acid, the corresponding *chloride*, $(Ta_6Br_{12})Cl_2,7H_2O$, is produced. The *iodide*, $(Ta_6Br_{12})I_2,7H_2O$, has also been prepared. Since in these compounds the complex Ta_6Br_{12} acts like a single element or base, it is proposed to term it "bromotantalum." The compounds which have been described receive the corresponding names of *bromotantalum bromide, hydroxide, chloride,* and *iodide.*

Chabrié's chloride (*loc. cit.*) has been found to be analogous to bromotantalum bromide, and is therefore to be regarded as chlorotantalum chloride, $(Ta_6Cl_{12})Cl_2,7H_2O$. E. G.

Optics of Colloidal Gold. LUIGI ROLLA (*Atti R. Accad. Lincei,* 1910, [v], **19**, i, 141—146).—By the action of glycerol, either alone or in presence of increasing amounts of potassium carbonate, on dilute gold chloride solution, the author has prepared colloidal gold solutions varying in colour from blue through violet to red, and in the number of granules from 4×10^7 per cub. mm. to zero. Spectrophotometric measurements show that Beer's law holds for the red solution in which no granules were observed (compare Scarpa, Abstr., 1908, ii, 244). The violet gold is further shown to be a mixture of the blue and red forms (compare Steubing, Abstr., 1908, ii, 600).

T. H. P.

Solubility of Gold in Nitric Acid. FREDERIC P. DEWEY (*J. Amer. Chem. Soc.,* 1910, **32**, 318—323).—It has been stated repeatedly that in parting gold from silver in assaying, some gold is liable to be dissolved by the nitric acid used. A study has now been made of this question, and the results of several experiments are recorded.

It has been found that, under certain conditions, gold does dissolve slightly in concentrated nitric acid. For example, if a small piece of gold is alloyed with 2·5—3 times its weight of silver, and the silver is afterwards removed by means of dilute nitric acid, the residual gold, if boiled for a few minutes with concentrated nitric acid, will dissolve sufficiently to furnish a distinctly yellow solution. The effect of the solubility of gold is negligible in ordinary ore assays unless the ores are unusually rich, but is of importance in the assay of bullion. E. G.

Preparation of Platinum-black. F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.,* 1910, **32**, 336—338).—Kastle and Elvove (Abstr., 1904, ii, 481) have found that platinum-black, prepared by precipitation with zinc, contains an appreciable amount of the latter metal, and that this affects its properties and is difficult to remove.

It is now shown that platinum-black, containing 96·5% of platinum, can be obtained by reducing a solution of platinic chloride with ordinary sheet aluminium. The product is a dull black, finely-divided powder, and appears to have considerable catalytic power.

E. G.

The Estimation of Osmium: Osmium Oxides and Chlorides. OTTO RUFF and FERD. BORNEMANN (*Zeitsch. anorg. Chem.*, 1910, **65**, 429—456).—Pure potassium osmate, $K_2OsO_4,2H_2O$, is prepared by fusing osmium with potassium hydroxide and nitrate, dissolving in water, precipitating with alcohol, and oxidising the product with chromic acid in a current of oxygen. The osmium tetroxide thus formed is passed into pure potassium hydroxide solution, the salt precipitated with alcohol, and dried in a vacuum.

Osmium may generally be estimated by reduction to the metallic state in hydrogen. The hydrated dioxide, however, loses water explosively at 100—150°, and must be previously heated at 200° in a sealed tube until decomposed, and then cooled in liquid air or solid carbon dioxide, the tube opened, and transferred to the reduction tube. Some chlorides and fluorides, however, must be first dissolved in alcohol and sodium hydroxide, and boiled for an hour; the precipitated hydroxide is then collected and washed. A part remains in a colloidal state in the filtrate, and may be brought down by forming a precipitate of barium sulphate. By boiling in perfectly neutral solution, however, the whole of the osmium may be precipitated. Heating should be continued for six hours, as otherwise the hydroxide decomposes explosively on drying. The precipitate, collected on an asbestos filter, is dried in a current of carbon dioxide charged with alcohol, and then heated at 250° in carbon dioxide, being weighed as osmium dioxide.

For the volumetric estimation, the osmium is oxidised with chromic acid, distilled into a receiver containing potassium hydroxide, and, after acidifying with sulphuric acid, potassium iodide is added and the liberated iodine titrated with thiosulphate. The solution of the chloride may also be decomposed by boiling with alkali hydroxide, acidified with sulphuric acid, and titrated with permanganate at 60° in presence of manganous sulphate. The metal or its oxides may be titrated with permanganate in hydrofluoric acid solution. The permanganate method is very suitable for determining the state of oxidation of the osmium when the proportion of metal is known.

Hydrated osmium dioxide, dried over sulphuric acid, has the approximate composition $OsO_2,2H_2O$. It oxidises gradually in air to the tetroxide. The anhydrous dioxide is bluish-black, massive portions resembling indigotin. It was not found possible to prepare Moraht and Wischin's osmic acid, H_2OsO_4 (Abstr., 1893, ii, 381).

Osmium tetrachloride, $OsCl_4$, is prepared by heating osmium to 650—700° in a slow current of chlorine, allowing the issuing vapours to cool slowly in a tube wrapped in asbestos. It forms black, metallic crusts, volatilises in a vacuum to a yellow vapour, and is not hygroscopic. Water decomposes it very slowly, forming osmium dioxide and hydrochloric acid.

Osmium trichloride, $OsCl_3$, is obtained when the temperature is raised to 1050° and the vapour cooled rapidly, but is then mixed with the tetrachloride. When ammonium osmichloride, $(NH_4)_2OsCl_6$, is heated at 350° in chlorine, a dark microcrystalline sublimate of the trichloride is obtained. It dissolves readily in water. Silver chloride only slowly precipitates a grey substance.

Osmium dichloride, $OsCl_2$, obtained by heating the trichloride to 500° under reduced pressure and cooling the vapour to $-50°$, forms a dark brown, insoluble powder. C. H. D.

Mineralogical Chemistry.

The Need of a Systematic Study of Optically Active Petroleums. LEO UBBELOHDE (*Ber.*, 1910, 43, 608—609).—Polemical. A reply to Rakusin (this vol., ii, 45). J. J. S.

The Mercury Minerals from Terlingua, Texas. WILLIAM F. HILLEBRAND and WALDEMAR T. SCHALLER (*Bull. United States Geol. Survey*, 1909, No. 405, 1—174).—An account is given of the chemical and crystallographic characters of kleinite, montroydite, terlinguaite, and eglestonite, repeating in greater detail that already published (Abstr., 1907, ii, 788). The associated minerals, calcite, gypsum, barytes, jarosite, calomel, and native mercury, are also described. L. J. S.

Composition and Optical Characters of Dolomite from Algeria. ARTHUR HUTCHINSON (*Rep. Brit. Assoc.* for 1908, 1909, 701).—Colourless, transparent crystals from Biskra gave on analysis:

FeO.	CaO.	MgO.	CO_2.	Total.
0·75	30·31	21·62	47·45	100·31

corresponding with $FeCO_3$ 1·22, $CaCO_3$ 54·09, $MgCO_3$ 45·20%. The refractive indices of the same material are:

	Li.	Na.	Tl.
ϵ	1·5002	1·5022	1·5042
ω	1·6767	1·6813	1·6855

L. J. S.

Alstonite. STEFAN KREUTZ (*Bull. Acad. Sci. Cracow*, 1909, 771—800).—Crystals of alstonite from Alston in Cumberland were examined in detail with respect to their crystallographic ($a:b:c=0·582:1:0·719$) and optical characters ($\alpha=1·5261$, $\beta=1·671$, $\gamma=1·671$; $2E=11°29'—12°44'$); the complex twinning is discussed. Analysis gave the following results, corresponding with the formula $7·6CaCO_3,7·7BaCO_3,SrCO_3$:

BaO.	CaO.	SrO.	MnO.	CO_2.	Total.	Sp. gr.
48·54	17·60	4·25	trace	29·41	99·80	3·707

The physical constants calculated on the assumption that the mineral is an isomorphous mixture of aragonite, witherite, and strontianite agree to a certain extent, although not completely, with the observed values. L. J. S.

Alstonite and Ullmannite from Durham. LEONARD J. SPENCER (*Min. Mag.*, 1910, **15**, 302—311).—The rare species alstonite and ullmannite, the latter new to the British Isles, were found in a fault-vein intersecting the Coal Measures at the New Brancepeth Colliery, near Durham. The material filling the vein consists mainly of massive barytes with some witherite; crystals of both of these minerals are described. Alstonite occurs as small, pseudo-hexagonal twinned pyramids on the barytes or on the witherite; the order of succession being (1) barytes, (2) witherite, and (3) alstonite, and it is clear that the two latter have been derived from the barytes. Analysis of the alstonite gave the following results, corresponding approximately with the formula $BaCa(CO_3)_2$:

BaO.	CaO.	SrO.	MnO.	Insol. (barytes).	Sp. gr.
52·3	18·0	nil	0·06	0·2	3·67

Ullmannite occurs as crystals of cubic or of octahedral habit, and with its good cubical cleavage and bright metallic lustre it closely resembles (except in its tin-white colour) the galena with which it is associated. It contains nickel (27·87%), antimony (over 52%), sulphur, and a trace of iron, but no cobalt or arsenic, and is thus pure NiSbS; D 6·70. The ullmannite and galena often form parallel intergrowths, their molecular volumes (31·5 and 31·9 respectively) being almost identical. L. J. S.

Minerals from the Pegmatites of Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1910, **33**, 37—53).—Further notes, mainly relating to occurrence and crystallographic details, are given respecting the following minerals from the pegmatite-veins of Madagascar (Abstr., 1909, ii, 57). Tourmaline; rhodizite (this vol., ii, 46); tabular crystals of pink beryl rich in alkalis (especially cæsium), to which the name worobeweite is applied (Abstr., 1909, ii, 955); garnets (grossularite, spessartite, and almandine); spodumene; bityite; felspars; lazulite, and hambergite. The last-named rare mineral is found as large crystals loose in the surface soil at Anjanabonoana [? Anjanabonsana]. Analysis by F. Pisani gave the following results, agreeing with the formula $4GlO,B_2O_3,H_2O$. Rather smaller crystals of hambergite are also found at Maharitra; these have hitherto been mistaken for spodumene:

GlO.	B_2O_3.	Na_2O,K_2O.	H_2O.	Total.
54·80	35·10	traces	10·95	100·85

L. J. S.

Variscite, from Vashegy, Hungary. KARL ZIMÁNYI (*Math. és természettud. Értesitő, Budapest*, 1908, **26**, 72—76; *Ber. aus Ungarn*, 1909, **25**, 241—245).—A pale apple-green mineral with a botryoidal surface encrusts black slate in an iron (chalybite) mine at Vashegy in

comitat Gömör. Thin sections under the microscope show a fine-grained aggregate with a concentric-shelly arrangement; the grains are birefringent; D 2·431; H 4—5. The following analysis by J. Loczka, agrees with the formula $Al_2O_3,P_2O_5,5H_2O$, that is, with one more molecule of water than is usually assigned to variscite:

Al_2O_3.	Fe_2O_3.	FeO.	Cr_2O_3.	CuO.	CaO.	MgO.	Na_2O.	K_2O.	P_2O_5.	H_2O.	Insol.	Total.
28·83	2·27	0·16	0·73	0 09	0·22	0·10	0·07	0·12	41·98	25·98	0·26	100·81

L. J. S.

[Wolframite and Apatite from Carrock Fell, Cumberland.] Alexander Moncrieff Finlayson (*Geol. Mag.*, 1910, [v], **7**, 19—28).—The quartz-veins of Brandy Gill, on the side of Carrock Fell, traverse greisen and carry wolframite (anal. I), scheelite, gilbertite (with 0·92% fluorine), pale yellow to green crystals of fluor-apatite (anal. II), mispickel, tetradymite, bismuthinite, etc.:

	WO_3.	FeO.	MnO.	CaO.	MgO.	Total.
I.	76·24	16·39	6·05	1·05	0·11	99 84

	P_2O_5.	F.	Cl.	CaO.	Al_2O_3.	Fe_2O_3.	MgO.	Total.
II	40·56	2·98	0 66	54·11	0·87	1·05	0·24	100·47

The different modes of occurrence of tungsten ores are discussed.

L. J. S.

A Variety of Minervite from Réunion. Alfred Lacroix (*Bull. Soc. franç. Min.*, 1910, **33**, 34—37).—A soft, white, powdery material, collected in 1822 in a basalt cave in the St. Paul district on the island of Réunion, gave the following analysis by F. Pisani. Under the microscope the material appears to be homogeneous, but it is without action on polarised light:

P_2O_5.	Al_2O_3.	Fe_2O_3.	K_2O.	$(NH_4)_2O$.	H_2O.	Total.
42·70	21·00	2·90	1·20	3·47	29·80	101·07

Formula: $2AlPO_4,(K,NH_4,H)_3PO_4,7\frac{1}{2}H_2O$. The material is, therefore, similar in composition to minervite (Abstr., 1896, ii, 529) and palmerite (Abstr., 1906, ii, 544), although it differs in containing more ammonium and less potassium. This difference is, however, not sufficient to warrant the giving of a new name to amorphous material.

L. J. S.

Carnotite and an Associated Mineral Complex from South Australia. Thomas Crook and George S. Blake (*Min. Mag.*, 1910, **15**, 271—284).—Carnotite occurs in small amount at Radium Hill, near Olary, in South Australia, as a yellow powder in the cracks and crevices of an intimate intermixture of ilmenite, magnetite, rutile, etc. Under the microscope it shows minute, rhombic plates with a perfect basal cleavage, which are orthorhombic in symmetry; perpendicular to the base is an acute negative bisectrix ($2E = 90°$ about). The carnotite from Colorado shows similar characters under the microscope. Material for analysis could only be obtained by dissolving the yellow powder from the fragments of gangue; deducting ferric oxide and alumina, and assuming the presence of 5% of water,

the re-calculated composition of the carnotite is given under I. Carnotite appears to be a definite mineral species, being essentially a hydrous vanadate of uranium and potassium, analogous to autunite (hydrous uranium calcium phosphate):

	U_3O_8.	V_2O_5.	P_2O_5.	CaO.	MgO.	K_2O.	Na_2O.	PbO.	H_2O.	Total.
I.	60·8	21·4	trace	1·3	trace	6·6	2·3	1·7	[5·0]	99·1
II.	2·25	0·93	—	0·25	,,	—	—	0·40	1·21	—

	TiO_2.	Fe_2O_3.	FeO.	SiO_2.	Cr_2O_3.	MnO.	ThO_2.	Ce_2O_3.	$(La,Di)_2O_3$.	Y_2O_3.	Total.
II.	51·85	17·87	17·37	1·21	1·60	0·24	0·13	1·26	2·13	1·15	99·85

Analysis of the associated complex gave II; D 4·33. Under the microscope it shows titaniferous magnetite (ilmenite + magnetite) and rutile, and in the crevices, carnotite and a brown, optically isotropic material, which is possibly tscheffkinite. The rutile (D 4·2) contains about 3% iron oxide and about $1\frac{1}{2}$% vanadic oxide, and may be described as a vanadiferous nigrine. This material is thus clearly a mixture of minerals, and the names "davidite" and "sefströmite" appear to have been applied to it in error. L. J. S.

[Adamite from Thasos, Turkey. "Barytocelestine," from Binnenthal, Switzerland.] VOJTĚCH ROSICKÝ (*Bull. Intern. Acad. Sci. Bohême*, 1909, **13**, 21—50).—Granular and columnar adamite occurs, together with barytes, in a brownish-yellow matrix containing arsenic, lead, zinc, iron, and some calcium; colourless or yellowish, etc., crystals line the cavities. The crystals are much intergrown and irregular, with vicinal faces [$a:b:c = 0·9764:1:0·7049$]. Analysis by H. Němeček gave:

As_2O_5.	ZnO.	FeO.	H_2O.	Total.	Sp. gr.
39·80	56·98	trace	[3·22]	100·00	4·484

These results agree closely with the usual formula, and the material being quite pure, the distortion in the crystalline growth cannot be attributed to isomorphous mixing.

The erroneous determination of "barytocelestine" from the white, crystalline dolomite of the Binnenthal has already been pointed out (Abstr., 1908, ii, 508). The crystals are really pure barytes, as shown by the following analysis by B. Kužma:

Ba.	Ca.	Sr.	SO_4.	Fe, Al.	Total.
58 54	0·16	nil	41·22	traces	99·92

"Barytocelestine" does not exist as distinct crystals, and the material analysed from other localities is probably only a mixture of barytes and celestite. L. J. S.

Occurrence of Salts at Hall, Tyrol. R. GÖRGEY (*Tsch. Min. Mitt.*, 1909, **28**, 334—346).—Specimens of granular rock-salt from the Salzberg at Hall were found to contain embedded nodules and grains of various alkali magnesium sulphates, together with small crystals of gypsum and anhydrite. *Langbeinite* ($2MgSO_4,K_2SO_4$) shows a conchoidal fracture with bright vitreous lustre, and is, in part, water-clear, but owing to absorption of water from the atmosphere it soon becomes crusted over with a mixture of picromerite ($MgSO_4,K_2SO_4,6H_2O$) and epsomite ($MgSO_4,7H_2O$). It gave analysis I;

$H > 4$; refractive index, 1·5347 (Na). Enclosed in the langbeinite are brick-red grains of halite, minute crystals of quartz and iron-pyrites, and small grains and crystals of anhydrite, the last being sometimes separated from the host by a zone of polyhalite ($2CaSO_4,MgSO_4,K_2SO_4,2H_2O$). In other specimens, the nodules embedded in the rock-salt consist of an intergrowth of langbeinite and blödite ($Na_2SO_4,MgSO_4,4H_2O$):

	MgO.	K_2O.	Na_2O.	SO_3.	Total.	Sp. gr.
I.	19·91	22·72	—	57·99	100·62	2·825
II.	7·37	—	33·64	58·54	99·55	2·694

Vanthoffite ($3Na_2SO_4,MgSO_4$; anal. II) was detected as a nodule embedded, together with löweite, in blödite. It is water-clear with a flat, conchoidal fracture and glassy lustre; $H = 3\frac{1}{2}$; refractive indices (Na), $\alpha = 1·4855$, $\beta = 1·4876$, $\gamma = 1·4893$. The löweite is reddish-yellow, with $D = 2·374$, $\omega = 1·4896$ (Na), $\epsilon = 1·4712$ (Na); it is rhombohedral and optically negative (not tetragonal and optically positive, as stated by Haidinger in 1846). L. J. S.

Gyrolite from Co. Antrim. FRIEDRICH N. A. FLEISCHMANN (*Min. Mag.*, 1910, **15**, 288—293).—The mineral gyrolite has not previously been recorded from Ireland. It is found at several places in the basaltic lavas near Belfast, where it is associated with various other zeolites (faroelite, apophyllite, chabazite, etc.). It occurs as small, hemispherical or spherical aggregates of pearly scales; it is optically uniaxial and negative; D 2·35—2·40. A partial analysis of material from Cat Carn gave:

SiO_2.	CaO.	Al_2O_3.	H_2O.	Total.
51·69	30·44	3·64	13·44	99·21

Water determinations of material from other localities gave 13·06 and 13·30%. L. J. S.

Benitoite, its Paragenesis and Mode of Occurrence. GEORGE DAVIS LOUDERBACK. With chemical analyses by WALTER C. BLASDALE (*Bull. Dept. Geol. Univ. California*, 1909, **5**, 331—380. Compare Abstr., 1907, ii, 705).—This interesting new mineral is found at a single locality in the Diablo Range, San Benito Co., California. It occurs, together with neptunite (syn. carlosite), in veins of natrolite, which traverse a large, lenticular mass of schistose rocks (largely soda-amphibole schists), embedded in serpentine.

The well-developed crystals of benitoite are trigonal, and afford the only known example, amongst minerals, of the ditrigonal-bipyramidal class; $a : c = 1 : 0·7344$. The largest crystal found is $2\frac{1}{2}$ inches across; $D = 3·64—3·67$; $H = 6\frac{1}{4}—6\frac{1}{2}$. Optically uniaxial and positive; $\omega = 1·757$, $\epsilon = 1·804$ (Na). The pleochroism is intense, the ordinary ray being colourless and the extraordinary ray greenish-blue to indigo-blue; the characteristic pale to deep blue colour of the mineral is thus entirely due to the extraordinary ray. Colourless crystals are rare, and colourless and blue portions sometimes occur in the same crystal. The mineral is practically insoluble in hydrochloric acid, but

is attacked by hydrofluoric acid. Analyses I and II are of blue crystals, and III of white material :

	SiO_2.	TiO_2.	BaO.	Total.
I.	43·56	20·18	36·34	100·08
II.	43·79	20·00	36·31	100·10
III.	43·61	19·50	37·01	100·12

The blue colour is possibly due to titanium, which is present only in the higher degree of oxidation ; no iron, cobalt, manganese, copper, or chromium could be detected. The formula $BaTiSi_3O_9$ represents a very acid titano-silicate.

A description is given of the lustrous, black, prismatic crystals of neptunite (Abstr., 1909, ii, 815). In thin splinters this mineral shows a deep blood-red colour ; D = 3·18—3·19.

The natrolite which forms the matrix of benitoite and neptunite occurs as granular masses, or as peculiar aggregates of tabular crystals ; it gave analysis IV.

Amphiboles of various types (actinolite, glaucophane, and crossite or crocidolite) occur as green or bluish-green needles in the natrolite veins. The type related to crossite gave anal. V :

	SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O (at 110°).	H_2O (ign.)	Total.
IV.	47·69	27·14	—	—	—	—	15·74	—	9·56		100·13
V.	52·94	3·76	13·40	1·44	11·54	5·45	5·11	0·43	1·31	3·72	98·67

The name *joaquinite* is applied to minute, honey-yellow or light brown, orthorhombic crystals found in the natrolite vein ; D 3·85 ; these contain silica, titanium, calcium, and some iron, but they have not yet been completely determined.

Other veins in the same rocks contain crystals of albite, and stellate groups of ægirite. L. J. S.

Solution of Heavy Vapours in Zeolites. F. GRANDJEAN (*Bull. Soc. franç. Min.*, 1910, **33**, 5—32).—Certain zeolites when dehydrated may absorb not only air, water, ammonia, etc. (Friedel, Abstr., 1896, ii, 481), but also vapours of iodine, bromine, mercury, calomel, cinnabar, or sulphur. Chabazite, for example, may take up as much as 27% of mercury. Chabazite, gmelinite, levynite, harmotome, and gismondine were experimented with in this direction, and examined in detail more especially with respect to the marked changes which their optical characters undergo. L. J. S.

Prismatine and Kryptotile from Waldheim, Saxony. J. UHLIG (*Zeitsch. Kryst. Min.*, 1910, **47**, 215—230).—Prismatine occurs, together with corundum, sillimanite, kyanite, andalusite, tourmaline, etc., in a granulite at Waldheim, in Saxony, from which locality it was described by A. Sauer in 1886. It had subsequently been identified with the Greenland mineral kornerupine. The orthorhombic crystals are small and prismatic in habit, and only rarely show terminal faces [$a:b:c = 0·8622:1:0·4345$]. The colour is yellowish-brown, in thin sections colourless ; D 3·345 ; refractive indices, $\alpha = 1·6711$, $\beta = 1·6826$, $\gamma = 1·6840$. The material is fusible only with

difficulty, and it is very slowly attacked by hydrofluoric or sulphuric acids. Analysis gave:

SiO_2.	TiO_2.*	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	Na_2O.	K_2O.	H_2O.	Moisture.	Total.
30·61	0·30	42·11	2·21	4·51	15·23	1·85	0·85	1·94	0·14	99·75

* Due to the presence of rutile.

The water is expelled only at a high temperature. Formula: $H_3NaMg_6Al_{12}Si_7O_{40}$, some of the magnesia being replaced by ferrous oxide and some of the alumina by ferric iron. Lorenzen's analysis (1884) of kornerupine reduces to the analogous formula: $H_2Mg_7Al_{12}Si_7O_{40}$, with Mg in place of HNa. Prismatine and kornerupine are therefore considered to be closely related and isomorphous, although distinct species.

Kryptotile, described by A. Sauer in 1886 as an alteration product of prismatine, is considered to be a compact variety of mica (compared with oncosine), but one in which all the alkalis are replaced by hydrogen, the formula being $H_3Al_3Si_3O_{12}$. L. J. S.

Mesolite. R. GÖRGEY (*Tsch. Min. Mitt.*, 1909, **28**, 77—106. Compare Abstr., 1909, ii, 677).—A detailed examination has been made of acicular crystals of mesolite from the Faroe Islands; these are 1—2 cm. in length and 0·3—0·5 mm. in thickness. They have the form of nearly square prisms with a perfect prismatic cleavage ($mm = 88°30'$) terminated by a low pyramid. The angular measurements conform closely with monoclinic symmetry ($a:b:c = 0·9747:1:0·3122$; $\beta = 92°$), but the optical characters prove that the crystals are really triclinic with interpenetrating twinning. Refractive indices (Na), $\alpha = 1·5048$, $\beta = 1·5050$, $\gamma = 1·5053$; the double refraction is thus very low. Optic axial angle $2V\gamma$, 82° (red), 86° (Na), 98° (blue). The optic orientation and the positive or negative sign vary with the temperature. Analysis gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.	Sp. gr.
46·50	26·58	9·72	4·97	12·29	100·06	2·272

These results correspond with a mixture of one molecule of natrolite with two of scolecite, namely,

$$Na_2Al_2Si_3O_{10},2H_2O + 2(CaAl_2Si_3O_{10},3H_2O).$$

Mesolite is, however, a double salt, and not an isomorphous mixture of natrolite and scolecite, as is indicated by the fact that it is triclinic, whilst the latter are both monoclinic, and the interfacial angles do not lie between the corresponding angles of natrolite and scolecite; this conclusion is also borne out by the optical characters. L. J. S.

Beryl from the Pegmatites of Madagascar. LOUIS DUPARC, M. WUNDER, and R. SABOT (*Bull. Soc. franç. Min.*, 1910, **33**, 53—67). —A description is given of crystals of rose-pink and blue beryl collected at various places in the neighbourhood of Antsirabé (Abstr., this vol., ii, 210). Rose-pink crystals of short, prismatic habit, and D 2·72, from Tsilaisina gave on analysis:

SiO_2.	Al_2O_3.	GlO.	MnO.	Li_2O.	Na_2O.	K_2O.	H_2O.	Total.
64·76	18·14	13·76	0·003	0·04	0·73	0·15	2·24	99·823

L. J. S.

Pilolite from China. G. STAFFORD WHITBY (*Min. Mag.*, 1910, 15, 294—298).—Thin, flexible sheets of "mountain leather" are found in rock-crevices at several places in the west of the province of Süchwan, near the Yunnan border. It is white and felt-like, and under the microscope is seen to consist of fine, interlaced fibres with a refractive index of about 1·5 and straight extinction. The material does not lose water in a vacuum-desiccator, but at 100° there is a loss of 6·06%, this amount being re-absorbed from moist air. Before the blowpipe, the mineral contracts and fuses. Analysis gave:

SiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	H_2O.	Total.
54·94	14·83	0·55	trace	10·94	18·12	99·38

corresponding with the formula $Al_2Si_2O_7,2MgSi_2O_5,7H_2O$.

The mineral is thus quite distinct from amphibole-asbestos and serpentine-asbestos. L. J. S.

Dyke Rocks in Northumberland. MARY KINGDON HESLOP and JOHN ARMSTRONG SMYTHE (*Quart. Journ. Geol. Soc.*, 1910, 66, 1—18).—The rock of the Crookdene dyke is a fine-grained basalt (anal. I) composed of felspar, augite, and grains of iron oxide; in it are large inclusions of felspar aggregates (anal. II, anorthite), which have evidently been brought up with the magma.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	H_2O.	Total.	Sp. gr.
I.	51·31	1·00	14·55	—	9·02	0·47	11·61	6·85	0·60	1·79	1·47	1·14	99·81	2·88
II.	45·88	0·04	34·31	0·83	—	—	18·28	—	0·11	0·82	—	1·14	100·41	2·703

L. J. S.

Crystallisation of a Basaltic Magma from the Standpoint of Physical Chemistry. CLARENCE N. FENNER (*Amer. J. Sci.*, 1910, [iv], 29, 217—234).—If no chemical change takes place within the mass from the time that the initial crystals appear until solidification is complete, the progress of crystallisation may be anticipated to be very regular. Each compound present has its temperature of solidification depressed according to the number of molecules of other substances present. The first mineral which separates is that present in greatest excess over the eutectic ratio; it is then joined by a second, and the composition of the solution approaches the eutectic ratio when it solidifies in the appropriate proportions. If, however, there is a sudden chill at any stage of the process, the great viscosity prevents further crystallisation and a glass is formed. These deductions from the principles of chemical equilibrium are shown to be valid by an investigation of the Watchung basalt, the three principal components of which, diopside, plagioclase, and magnetite, appear to be present in approximately the eutectic ratio.

Another phenomenon observed in these basalts is the partial resorption of olivine, which separates out at an early stage of crystallisation, and is partly or completely redissolved at a later stage. This may be due, in part at least, to displacement of the equilibrium as the temperature and pressure alter. G. S.

Minerals from the Radauthal, Harz. JOHANNES FROMME (*Tsch. Min. Mitt.*, 1909, **28**, 305—328).—*Greenockite* forms a thin, yellow dusting on calcite in association with prehnite, blende, etc., on the Radauberg.

Nephritoid (anal. I), a compact, pale greyish-green mineral, resembling nephrite in appearance, forms a vein in weathered harzburgite. It differs from true nephrite in having a parallel arrangement of its fibres (as seen under the microscope) instead of a matted arrangement; it may thus be considered to be a compact actinolite.

Rhodonite (II) occurs as amygdaloidal masses embedded in the gabbro; it is granular with a rose-red colour, and is associated with manganiferous garnet, tourmaline, pyrrhotite, etc.

Axinite (III) occurs as thin, platy crystals, with a pale greenish-grey or sometimes bluish colour, associated with quartz, prehnite, and delessite in pegmatite. Analysis proves it to be a mangan-axinite, with the formula $HMnCa_2BAl_2Si_4O_{16}$.

Datolite (IV), granular, from gabbro; formula, $Ca(B,Al)OH(SiO_4)$.

Apophyllite (V): small crystals occurring with prehnite, calcite, and quartz in pegmatite. When heated, the mineral gives off ammonia. The alumina shown in the analysis is not due to the presence of impurity. Formula: $K_2H_8Si_3O_{11} + 4Ca_2H_6Si_3O_{11}$.

Mesolite (VI): a white, fibrous zeolite, occurring with stilbite, laumontite, analcite, apophyllite, and calcite. The analysis corresponds with 1 molecule of scolecite + 1·6 molecules of natrolite, but the bases are slightly in excess.

Orthite (VII): several well-developed crystals have been found in the pegmatite. Full details of the method of analysis are given:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	56·22	0·51	0·49	5·67	trace	17·33	15·71	—	—	2·95	98·88	2·986
II.	48·24	0·46	—	0·95	33·41	14·18	2·42	—	—	—	99·66	3·387
III.	41·73	17·08	1 87	1·35	11·54	18·65	0·34	—	—	1·81	100·67*	3·313
IV.	37·65	1·18	—	—	—	34·91	—	—	—	5·90	100·43†	2·951
V.	52·15	1·78	0·02	—	—	24·16	0·24	4·02	0·73	16·57	100·15‡	2·364
VI.	45·63	26·60	—	—	—	5·20	0·40	0·90	9·67	11·95	100·35	2·279
VII.	31·90	14·18	5·35	11·67	trace	8·88	0·31	1·19	1·36	2·87	100·30§	3·706

* Including B_2O_3, 6·30. † Including B_2O_3, 20·79.
‡ Including F, 0·29; $(NH_4)_2O$, 0·19.
§ Including Y_2O_3, 0·21; Ce_2O_3, 11·23; $(Nd,Pr,La)_2O_3$, 10·73; GlO, 0·42.

L. J. S.

Manganese Minerals from Veitsch, Styria. ADOLF HOFMANN and FRANTIŠEK SLAVÍK (*Bull. Intern. Acad. Sci. Bohême*, 1909, Reprint 10 pp.).—The deposits of manganese ore at Veitsch occur in crevices in Silurian limestones, and were formerly extensively mined. The ore consists mainly of rhodochrosite, together with rhodonite and friedelite, and, in smaller quantities, garnet, manganophyllite, neotocite, manganiferous calcite, and an emerald-green chrome-mica. The granular admixtures of these minerals are of the nature of rocks.

Friedelite occurs in considerable quantity as veins and pockets in

the rhodochrosite, or as a granular rock intermixed with the other minerals. It is granular to lamellar in texture, with a pale yellowish-brown to chestnut-brown colour; rhombohedral crystals are rare; D 3·067. Optically, it is uniaxial or biaxial ($2E = 20\frac{1}{2}°$). Analyses by F. Kovár gave (I) for pure brown cleavage flakes; and (II) for the finely granular, reddish material.

	SiO_2.	MnO.	FeO.	CaO.	MgO.	H_2O.	Cl.	Total (less O for Cl).
I.	33·29	56·94	trace	0 76	0·64	8·08	1·16	100 61
II.	32·87	56·11	,,	1·68	1·53	7·91	0·37	100·38

Of the water, 3·56% is lost in the desiccator, the remainder only on ignition. Analysis I corresponds with the formula $(H,Cl)_8R_7Si_5O_{21}$, and II with $(H,Cl)_8R_8Si_5O_{22}$. The differences between these and the usually accepted formula of friedelite is perhaps due to a slight alteration of the mineral. L. J. S.

The Ancient Lavas in the Neighbourhood of Cracow. Z. ROZEN (*Bull. Acad. Sci. Cracow*, 1909, 801—859).—In a petrographical description, with several rock analyses, the following mineral analyses are also given. (I) Biotite, isolated from the porphyry of Zalas; (II) hypersthene, from the hypersthene-diabase of Niedźwiedzia Góra; (III) a green, earthy alteration product (showing under the microscope a fibrous structure), occurring in cavities of the melaphyre of Mirów. (IV) white, spherical masses with fibrous structure, occurring in cavities of the melaphyre of Rudno; this appears to be allied to pilolite.

	SiO_2	TiO_2.	Al_2O_3	Fe_2O_3	FeO	MnO.	CaO	MgO.	K_2O.	Na_2O	H_2O (<110°).	H_2O (>110°)	Total.
I.	37 66	3 92	17 67	18 41	—	0 36	2 68	6 93	6 53	1 97	—	1 60	101 49*
II	49·49	2 22	1 36	3·58	20 71	1 09	6 26	14 47	0 15	0 45	0 15	0 55	100·48
III	49 58	0 37	9 08	10 53	0·46	trace	trace	7 24	n d	n d	11 53	8 68	97 47
IV.	48·71	nil	6·40	2 93	0 18	0·14	1 61	16 17	0 27	2 11	12·88	8 39	99 79

* Including insoluble in HCl, 3·76

L. J. S.

Meteoric Stone from Simondium, Cape Colony. GEORGE T. PRIOR (*Min. Mag.*, 1910, **15**, 312—314).—Two "boulders" were found in gravel at a foot beneath the surface. The much rusted material consists mainly of enstatite, olivine, and plagioclase-felspar, with magnetite, nodules of troilite, and particles of nickel-iron. The characters are those of the howardite group of Brezina, and they approach those of terrestrial basalts; but the fact that no basaltic rocks occur in the neighbourhood of the find adds support to the meteoric origin of the masses. Analysis of the olivine gave:

SiO_2.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
39·22	2·59	8·26	48·79	0·47	99·33

L. J. S.

Angra dos Reis Meteorite. ERNST LUDWIG and GUSTAV TSCHERMAK (*Tsch. Min. Mitt.*, 1909, **28**, 110—114).—This meteoric stone consists of augite (92·89%), olivine (5·55%), pyrrhotite (1·26%), opaque, glassy particles, and grains of apatite (0·30%). W. Wahl

has recently pointed out that the augite strikingly resembles in its optical characters the titaniferous augite of certain basaltic rocks. A determination of the titanium dioxide in the stone gave 2·39%, and of phosphoric oxide, 0·13%. The analysis published in 1887 (in which the titanium was overlooked) therefore requires correction (I). Under II is given the calculated composition of the augite; the composition of this is expressed as a mixture of the molecules: Si_2MgCaO_6, Si_2FeCaO_6, $SiAl_2CaO_6$, $TiAl_2CaO_6$, and Si_2FeNaO_6.

	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	Fe.	S.	Cr.	Total.
I.	43·94	2·39	0·13	8 73	0 31	8·28	10·05	24 51	0·26	0·19	0·81	0 45	trace	100·05
II.	45·28	2·57	—	9·40	0·33	7·48	9·63	24 83	0 28	0·20	—	—	—	100·00

L. J. S.

Physiological Chemistry.

Influence of Temperature on Vital Processes. ARISTIDES KANITZ (*Zeitsch. physikal. Chem.*, 1910, 70, 198—205. Compare *Zeitsch. Elektrochem.*, 1907, 13, 707).—Further instances are cited in which the rule, applicable to chemical changes, that the velocity is doubled or trebled for a rise of temperature of 10°, has been shown to be applicable also to vital processes. Moreover, from the data of Nägeli, Czapek, Bach, and other botanists, it is shown that the same rule holds within certain limits for the rotation of protoplasm, and for the geotropic phenomena of plants. In most of the cases cited, the temperature-coefficient is much greater in the neighbourhood of 0°.

G. S.

Effect of Oxygen Inhalation on Muscular Exertion. LEONARD E. HILL and JAMES MACKENZIE (*Proc. physiol. Soc.*, 1909, xxxiii—xxxv; *J. Physiol.*, 39).—Further experiments on athletic exercises which the authors consider demonstrate the beneficial effect of oxygen inhalation.

W. D. H.

The Alveolar Carbon Dioxide Pressure in Disease. MABEL PUREFOY FITZGERALD (*J. Path. Bact.*, 1910, 14, 328—343).—During rest, the carbon dioxide pressure in the alveoli is normal or nearly so in various forms of anæmia, and in most diseases of the circulatory and respiratory organs. In congenital heart disease it is lower. There is thus at rest an adaptation to the altered conditions. At a high altitude such an adaptation does not succeed, and in carbon monoxide poisoning there is insufficient time for the adaptation to take place.

W. D. H.

The Oxygen Capacity of the Blood after Hæmorrhage. C. GORDON DOUGLAS (*J. Physiol.*, 1910, 39, 453—460).—The parallel relationship of colour and oxygen capacity of the blood is not materially disturbed during regeneration following repeated hæmorrhage in

rabbits. This supports the theory that there is only one kind of hæmoglobin, or, at least, that hæmatin is identical in all varieties of hæmoglobin. In the shed blood of such rabbits there is a rapid disappearance of oxygen and output of carbon dioxide.

W. D. H.

A Method for Determining the Alkalinity of the Blood. ARTHUR E. BOYCOTT and R. A. CHISOLM (*Bio-Chem. J.*, 1910, 5, 23—31). —The determination of the alkalinity of the blood by titration with acids and use of the ordinary indicators is very uncertain, because of the lack of sharpness of the end-point in the presence of proteins. A more precise method has been worked out, which depends on the appearance of a flocculent precipitate when a definite amount of acid is added to a solution containing a measured quantity of blood. A series of small tubes are prepared containing quantities of *N*/1000-sulphuric acid, rising by 0·1 c.c. from 0·0 to 1·2 c.c., the volume in each case being made up to 2 c.c. with distilled water. A drop (0·02 c.c.) of blood is then added to each tube, the contents well mixed, and the tubes placed in a water-bath at 45° for one hour. With average human blood the tubes containing the smaller amounts of acid show a slight opalescence, but a coarse, flocculent precipitate makes its appearance when the tubes containing 0·7—0·9 c.c. of acid are reached. The appearance of this precipitate is considered to indicate the neutralisation point.

The reaction is given equally well by fresh, defibrinated, oxalated or citrated blood, and by red corpuscles washed many times with salt solution. It is not given by citrated or oxalated plasma, by serum, or by a solution of fibrin. It is supposed that the precipitate consists of the nucleo-protein of red cells. H. M. D.

Transfusion. ARTHUR E. BOYCOTT and C. GORDON DOUGLAS (*J. Path. Bact.*, 1910, 14, 294—327).—The mechanism by which a rabbit trained by transfusion disposes of foreign corpuscles at the rate of 1 to 2 grams of hæmoglobin a day does not differ qualitatively from that by means of which the normal animal destroys an unknown, but much smaller, quantity of its own "effete" red cells. Presumably they are broken up in the spleen, where much of the iron remains; the iron-free pigment appears as urobilin in the urine. Possibly bile pigment is an intermediate stage in the formation of this pigment. There appears to be no direct hæmolysis in the circulation. W. D. H.

The Fate of Hen's Corpuscles when Injected Intravenously in Rabbits. J. P. McGOWAN (*J. Path. Bact.*, 1910, 14, 379—394).—The washed red corpuscles of the hen when injected intravenously into a rabbit, the serum of which lyses them *in vitro*, are rapidly dissolved in the circulating plasma without the intervention of phagocytosis. The complement is probably free in the plasma. Further, when they are so injected, especially when the serum is not lytic, they tend rapidly to accumulate in the liver, disappearing meanwhile from the blood and

spleen. This and other considerations suggest that the liver is the seat of formation of the immune substance. W. D. H.

The Equilibrium between Varying Concentrations of Acids and Alkalis and the Proteins of the Serum and other Colloids: The Nature of Colloidal Reaction or Adsorption. BENJAMIN MOORE and A. DOUGLAS BIGLAND (*Bio-Chem. J.*, 1910, 5, 32—78).—A dialytic method of determining the equilibria between serum proteins and acids or alkalis is described, in which a definite quantity of standard acid or alkali is added to a known volume of serum contained in a parchment dialysis tube immersed in a measured volume of water. After a sufficient time-interval has elapsed for the attainment of equilibrium, a known volume of the outer liquid is titrated. Since the concentration of free acid or alkali within and without the dialyser is the same, the amount of acid combined with protein can be calculated.

The experimental results indicate that the amount of acid or alkali united with the protein increases with the concentration of the total acid or alkali, and that a maximum is reached in both cases. This maximum is reached when the concentration of the acid or alkali is about 0·006 to 0·007*N*. The amount of acid combined with the protein is approximately twice that of the combined alkali. If the osmotic equivalent of the serum proteins is taken as 40,000, the experimental data indicate that each solution aggregate of protein can unite with about 60 molecules of acid or 30 molecules of alkali. The interval between the limits of the combining power of protein for acid and alkali corresponds approximately with the total amounts of crystalloid contained in the plasma, and this is supposed to afford evidence of a labile union between crystalloids and serum proteins.

In the second part of the paper the nature of the equilibrium between colloids and crystalloids is discussed. Although the phenomena met with in connexion with such equilibrium conditions exhibit characteristics which are supposed to be typical of adsorption phenomena, the authors consider that chemical affinity between the colloids and crystalloids plays a very considerable part. H. M. D.

Serological Studies with the Help of the Optical Method. IV. EMIL ABDERHALDEN and LUDWIG PINCUSSOHN (*Zeitsch. physiol. Chem.*, 1910, 64, 100—109).—After the parenteral administration of protein or peptone, the blood-plasma of the dog contains an enzyme capable of cleaving protein material which is not specific. Thus, if gelatin is injected, the enzyme breaks up, not only gelatin or gelatin-peptone, but also silk peptone. The similar administration of fat or carbohydrate does not give rise to the origin of peptolytic enzymes. In the case of injection of silk-peptone, the property of the blood disappears in about three weeks. No anaphylaxis was observed. In accordance with the known fact that overfeeding on protein is followed by the absorption of unchanged protein, it was found that overfeeding on eggs produced the development in the blood of a peptolytic enzyme. After this injection of silk peptone, the dialysate of the serum gives

an intense biuret reaction. The activity of the enzymes was detected throughout by the optical method. W. D. H.

Serological Studies by the Help of the Optical Method. V. EMIL ABDERHALDEN and K. B. IMMISCH. VI. E. ABDERHALDEN and A. ISRAËL. VII. E. ABDERHALDEN and J. G. SLEESWYK. VIII. E. ABDERHALDEN and CARL BRAHM. IX. E. ABDERHALDEN and LUDWIG PINCUSSOHN (*Zeitsch. physiol. Chem.*, 1910, **64**, 423—425, 426, 427—428, 429—432, 433—435).—V., VI., and VII.—These papers give further details concerning the non-specificity of the enzymes which appear in the blood as the result of the parenteral administration of proteins and peptones. Normal blood contains no such enzymes.

VIII.—After the similar parenteral administration of carbohydrates (starch, sucrose, lactose), enzymes develop in the blood which are capable of hydrolysing these carbohydrates.

IX.—Parenteral administration of iodised peptone does not give rise to enzymes in the blood capable of cleaving either ordinary or iodised peptone. In contradistinction to the dog, normal guinea pig's blood already contains enzymes capable of cleaving peptone. W. D. H.

The Rate of Inactivation of the Precipitable Substance by Alkalis. W. A. SCHMIDT (*Biochem. Zeitsch.*, 1910, **24**, 45—52).—It was found that relatively small concentrations of sodium hydroxide are sufficient to destroy horse-serum proteins in such a way that they no longer give the biological precipitin reaction; $N/40$-alkali, for example, can destroy the reaction if kept with the serum at room temperature for seven hours. Compared with the alkali hydroxides, the action of sodium carbonate or of ammonia is very small.

S. B. S.

Influence of Temperature on the Decomposition of "Anti-" Substances (Agglutinins). THORVALD MADSEN and OSV. STRENG (*Zeitsch. physikal. Chem.*, 1909, **70**, 263—276).—The measurements were made by methods described in previous papers. Sera containing coli and typhus agglutinins, obtained from goats and rabbits rendered immune by injection of coli and typhus cultures, were used.

The rate of loss of activity on heating of coli agglutinin from goats is in most cases represented by the unimolecular formula, and the same holds in some cases for the coli agglutinin from rabbits. Usually, however, the decomposition of coli agglutinin from rabbits, and typhus agglutinin from goats and rabbits, does not follow the unimolecular formula, being much slower towards the end of the reaction than the law requires. The rate of loss of activity of coli agglutinin in normal goat's serum follows the unimolecular formula. The rate of the reaction is retarded by diluting the agglutinin. Most of the experiments were made in the neighbourhood of 70°.

The dependence of the rate of loss of activity on the temperature has been investigated at different temperatures between 70·3° and 74·8°, and is satisfactorily represented by the Arrhenius formula: $\log_e(K_1/K_2) = \mu/2.(T_1 - T_2)/T_1T_2$. The value of μ for coli agglutinin from goats amounted in two experiments to 106,500 and 93,400; for the same agglutinin from rabbits, to 109,600. G. S.

Composition of the Egg in Relation to Biological Questions. I. Dextrose in the Egg: Its Condition in the White and in the Yolk. VINCENZO DIAMARE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 319—331).—After discussing the literature concerning the occurrence of dextrose in the egg, the author describes his own experiments, which show that the greater part of the dextrose of the white, and the whole of that of the yolk, of hen's eggs is present in the free state. The existence in the egg of a diastatic enzyme (compare Müller and Masuyama, Abstr., 1900, ii, 420; Roger, *J. Physiol. Path. gen.*, 1908, 797—804) is confirmed, the enzyme being isolated and its action on starch examined. T. H. P.

The Action of Radium Emanations on the Development of Animal Eggs. OSCAR HERTWIG (*Sitzungsber. K. Akad. Wiss., Berlin*, 1910, 221—233).—Exposure of frogs' eggs to radium emanations leads after a variable period (depending on length of exposure, stage the egg had already reached, and other factors) to pathological changes, which lead in the early stages to destruction of the egg, or to the development of "monsters." Exposure of the spermatozoa of frog and sea-urchin to radium rays does not prevent them fertilising the ovum, but, later on, pathological changes in the embryos are seen of a similar kind. W. D. H.

Nature of the Stimulus Leading to Development of the Animal Egg. JACQUES LOEB (*Zeitsch. physikal. Chem*, 1910, **70**, 220—229).—A brief account of the author's well-known work on parthenogenesis. It is suggested that in the resting unfertilised egg, more particularly near the surface, there is a solid substance, the swelling or dissolving of which constitutes the stimulus to development. In many, but probably not in all, cases this solution phenomenon is accompanied by membrane formation. To the question as to how the swelling or dissolving of this substance starts the development of the egg, no definite answer can at present be given. G. S.

Alkalinity of Saliva. RAGNAR BERG (*Zeitsch. physiol. Chem.*, 1910, **64**, 67—72).—Polemical. Röse's method for estimating the alkalinity of saliva is defended against the criticisms of Molen and Offringa (*Biochem. Zeitsch.*, 1909, **15**, 350). The alkalinity is due to diphosphates (1/10), hydrogen carbonates (2/10), and organic bases (7/10). These can only be accurately estimated if litmus is used as indicator. Methyl-orange is wholly unsuitable, and gives results which are too small, and which are not concordant. W. D. H.

Physiology of Digestion in New-Born Infants. JUSSUF IBRAHIM (*Zeitsch. physiol. Chem.*, 1910, **64**, 95—99).—The gastric juice of new-born infants contains a lipase which acts energetically on finely emulsified fats. The act of sucking calls forth saliva secretion reflexly in the first days of life, and this saliva contains a diastatic enzyme which in activity differs but little from that secreted later in life; it, however, contains no potassium thiocyanate, and probably no maltase. W. D. H.

Effect of Castration on Metabolism. FRANCIS H. McCRUDDEN (*J. Biol. Chem.*, 1910, **7**, 185—198).—Experiments on dogs do not confirm the view generally held that castration is followed by a general retention of material, especially in the mineral constituents of the body. The results show a general tendency in the opposite direction. This also is an argument against the view that osteomalacia is a disease of the ovaries. W. D. H.

Cardiac Metabolism of Alcohol. PHILIP HAMILL (*J. Physiol.*, 1910, **39**, 476—484).—A method of estimating alcohol in dilute solutions is described. It depends on the fact that in the presence of a moderate concentration of sulphuric acid and slight excess of chromic acid, alcohol is oxidised quantitatively to acetic acid and no further. If isolated rabbits' hearts are perfused by Locke's method, the addition of a small amount of alcohol to the perfusing fluid improves the beat, and the alcohol disappears (32 to 44% in different experiments). There is, therefore, ground for believing that the heart is capable of using alcohol within certain limits. W. D. H.

The Influence of Lecithin on Metabolism. S. YOSHIMOTO (*Zeitsch. physiol. Chem.*, 1910, **64**, 464—478).—Slowtzoff has shown that lecithin in man causes a retention of nitrogen and phosphorus. The present experiments on a dog with commercial preparations of lecithin confirm these results. W. D. H.

The Catabolism of Amino-acids in the Organism. LEOPOLD FLATOW (*Zeitsch. physiol. Chem.*, 1910, **64**, 367—392).—In the rabbit, *o*-tyrosine and *o*-hydroxyphenylpyruvic acid are broken down into *o*-hydroxyphenylacetic acid. The lactone of *o*-hydroxyphenylpyruvic acid is not split, but unites with glycuronic acid. The corresponding meta-compounds lead to the formation of *m*-hydroxyphenylacetic acid. By feeding on *m*-tyrosine, *m*-hydroxyphenylpyruvic acid is directly detectable in the urine. Feeding on the hitherto unknown *m*-chlorophenylalanine leads to the abundant appearance of *m*-chlorophenylpyruvic acid in the urine; *m*-chlorophenyl-lactic acid is not oxidised in the body to *m*-chlorophenylpyruvic acid. The hitherto unknown furylalanine leads to the formation of what is probably furylpyruvic acid. In the urine of a case of alcaptonuria, neither quinolpyruvic acid nor a ketonic acid could be detected.

The *lactimide* of m-*chloro-a-benzoylaminocinnamic acid*,

$$C_6H_4Cl\cdot CH{:}C<\begin{matrix}CO\\ |\\ N\cdot COPh\end{matrix},$$

is obtained by the condensation of *m*-chlorobenzaldehyde with hippuric acid in presence of sodium acetate and acetic anhydride; on alkaline hydrolysis it yields m-*chloro-a-benzoylaminocinnamic acid*, which was not further investigated, but converted by treatment with sodium amalgam into *benzoyl*-m-*chlorophenylalanine*, which crystallises in prisms terminated by pyramids, m. p. 174°. By treatment with hydrochloric acid, this is resolved into m-*chlorophenylalanine*, crystallising in colourless needles, m. p. 234°.

By a similar series of reactions, the *lactimide* of *benzoylaminofuryl-*

acrylic acid, $C_4OH_3\cdot CH:C<\begin{smallmatrix}C\\|\\N\cdot COPh\end{smallmatrix}$, yellow needles, m. p. 170°, and *benzoylfurylalanine*, $C_4OH_3\cdot CH\cdot CH(NHBz)\cdot CO_2H$, prisms, m. p. 163°, were obtained. As the benzoyl derivative is resinified when treated with acids, alkaline hydrolysis was employed, and *furylalanine* was eventually obtained in colourless prisms, m. p. above 240°.

W. D. H.

The Nutritive Value of Protein Cleavage Products. XII. EMIL ABDERHALDEN and OSKAR FRANK (*Zeitsch. physiol. Chem.*, 1910, **64**, 158—163).—Two further experiments on dogs show that these animals can maintain their nitrogenous equilibrium on the final cleavage products of meat; in the first case, hydrolysis was brought about by the combined action of pepsin, trypsin, and erepsin for three months; in the second case, by the action of sulphuric acid. The sickness and diarrhœa described in earlier experiments are probably due to traces of barium, and can be avoided by carefully removing these. It is also advantageous in experiments with the hydrolytic products obtained by acid to add tryptophan, as this substance is altered by the action of acid. W. D. H.

Comparative Study of Protein Cleavage in the Stomach. ARTHUR SCHEUNERT (*Festschrift Otto Wallach*, 1909, 584—630).—The anatomical variations in the stomach, from the simple stomach of the carnivore to the many-chambered stomach of the ruminant (and intermediate conditions between these extremes occur in the animal kingdom), are associated with differences in digestion. The pig takes a mid position between the pure carnivore and the herbivorous animal. In the two-chambered stomach of the hamster, one compartment is not antiseptic, and bacterial cleavage of proteins occurs. Other characteristic differences in various classes in reference to the rate of protein cleavage and other data are noted in full. W. D. H.

Nutritive Value of Blood Proteins. T. IMABUCHI (*Zeitsch. physiol. Chem.*, 1910, **64**, 1—9).—Defibrinated ox-blood was coagulated by heat, dried, powdered, and used in metabolic experiments on dogs. The body-weight, together with the nitrogen in urine and fæces, are recorded daily. About 86% of the nitrogen administered was absorbed, as compared with 94% before and after the use of the dried blood. The body during the feeding on blood exhibited a loss of nitrogen. The amount of creatinine secreted daily fell to about half the normal quantity. W. D. H.

The Purine Metabolism of the Monkey. H. GIDEON WELLS (*J. Biol. Chem.*, 1910, **7**, 171—184).—The paper contains a useful summary as to the differences which have been noted between animals as regards the activity of their tissue extracts in relation to purine metabolism. The monkey so far has not been particularly studied. The liver of *Macacus rhesus* destroys uric acid *in vitro*, but no other tissue is uricolytic. Man still remains the only mammal whose tissues are unable to destroy uric acid *in vitro*. The monkey, however, resembles man in that the liver and no other tissue contains xantho-

oxydase; it is also by the same or another oxydase able to convert hypoxanthine with xanthine. The liver and other viscera contain adenase, guanase, and nuclease. Monkey's urine contains very little purine nitrogen; uric acid was absent, except in one case of tuberculosis; allantoin is probably present in small amount. W. D. H.

Influence of the Removal of Fragments of the Intestinal Tract on the Character of Nitrogen Metabolism. II. The Removal of the Small Intestine. A. CARREL, GUSTAVE M. MEYER, and PHŒBUS A. LEVENE (*Amer. J. Physiol.*, 1910, **25**, 439—455).—After the removal of the greater part of the small intestine in dogs, the absorption of protein and of leucine is lessened. The rate of assimilation and of retention of absorbed protein follows, however, a normal course. Comparison with animals after gastro-enterostomy suggests that the stomach and not the intestines is the organ chiefly concerned in protein assimilation. W. D. H.

The Influence of Dietary Alternations on the Types of Intestinal Flora. CHRISTIAN A. HERTER and ARTHUR I. KENDALL (*J. Biol. Chem.*, 1910, **7**, 203—236).—In kittens and monkeys the change from a protein-rich to a sugar and milk diet is followed by a change in the nature of the intestinal flora, in the putrefactive products of urine and fæces, and in the clinical conditions. The chief bacterial change is the substitution of an acidophilic non-proteolysing type for a strongly proteolysing one. There is a reduction in indole, scatole, phenol, and bound hydrogen sulphide in the fæces, and of the indican and aromatic hydroxy-acids in the urine. Clinically there is an improvement in the animal's well being. Diminution of protein is only one factor, increase of carbohydrate is another. W. D. H.

The Relation between the Physical, Chemical, and Electrical Properties of Nerves. III. Total Ash, Sulphates, and Phosphates. NATHANIEL H. ALCOCK and G. ROCHE LYNCH (*J. Physiol.*, 1910, **39**, 402—410).—The following figures give percentages of the original weight of the horse's median and splenic nerves.

	Median nerve.	Splenic nerve.	Connective tissue.
Total ash	0·985	0·914	0·549
Sulphates	0·011	0·065	0·081
Phosphates	0·768	0·349	0·079
Total sulphur as SO_4	0·358	0·331	0·260
Total phosphorus as PO_4	0·781	0·404	0·130

There is, however, good reason to suppose that in no case do the percentages represent the amount of electrolytes in the original tissue, and that the analysis is of little assistance in the problem which is to be ultimately investigated. W. D. H.

Catalytic Acceleration of the Absorption of Oxygen by Muscle. T. THUNBERG (*Zentr. Physiol.*, 1909, **23**, 625—629).—Experiments with the author's microrespirometer show that when finely divided muscle has been treated with dilute ferric chloride

solution (0·16—1·6%), the rate at which it evolves carbon dioxide is diminished, the diminution being more marked the greater the concentration of the ferric chloride. At the same time the absorption of oxygen is increased, except when the most dilute solution (0·16%) has been employed. The substance which undergoes oxidation can be extracted with alcohol. The same behaviour is shown both by living and by dead muscle, also by egg-yolk and by lecithin preparations.

R. V. S.

The Formation of Creatine in Muscle in Tonus and Rigor. CORNELIS A. PEKELHARING and C. J. C. VAN HOOGENHUYZE (*Zeitsch. physiol. Chem.*, 1910, **64**, 262—293).—Creatine was estimated by first converting it into creatinine, and then carrying out the colorimetric test. In heat coagulation, in rigor mortis, in decerebrate rigidity, and in tonus (as compared with toneless muscles, their nerves having been divided), a chemical change occurs which leads to an increase in the amount of creatine in the muscle. The experiments were performed on frogs and rabbits. W. D. H.

The Action of the Proteins of the Blood on the Isolated Mammalian Heart. L. W. GORHAM and A. W. MORRISON (*Amer. J. Physiol.*, 1910, **25**, 419—432).—The blood proteins added to the circulating fluid, as in Locke's method, have no favourable action such as dextrose has in sustaining the beat of the isolated cat's heart. It is not clear whether they are injurious. Fibrinogen causes a temporary inhibition; on serum-globulin the heart beats poorly. Serum-albumin has no effect, and is not used by the heart. The other two proteins, on the other hand, gradually diminish in the circulating fluid; they are supposed, therefore, to be used in some way by the heart. W. D. H.

The Iron-content of the Liver after Feeding on Ferratin. T. IMABUCHI (*Zeitsch. physiol. Chem.*, 1910, **64**, 10—15).—After feeding rabbits on ferratin, the percentage of iron in the liver rose to 14·08 mg. in 100 grams of liver, as compared with 11·15 in control animals. W. D. H.

The Depression of the Ammonia-destroying Power of the Liver after Complete Thyroidectomy. ANTON J. CARLSON and CLARA JACOBSON (*Amer. J. Physiol.*, 1910, **25**, 403—418).—In completely thyroidectomised cats and foxes which exhibit the typical symptoms so produced, the ammonia rises in the blood above the normal, especially in foxes; this is associated with a marked depression of the ammonia-destroying power of the liver, and this is held to be the main cause of the rise of ammonia in the blood.

W. D. H.

Reductase in Liver and Kidney. D. FRASER HARRIS (*Proc. physiol. Soc.*, 1909, xxiv–xxv; *J. Physiol.*, **39**)—The press juice of sheep's liver and ox kidney contains a reductase which will reduce Prussian-blue to the pale green or colourless chromogen, and sodium sulphindigotate

and methylene-blue to the pale green condition. The enzyme is soluble in glycerol, is partly destroyed by alcohol or by drying, acts most energetically at 40—50°, and is destroyed at 100°. The cell-proteins with which it is intimately associated shield it somewhat from the effect of heat. It is precipitated with the cell-proteins by ammonium sulphate. W. D. H.

Uric Acid Formation. V. GUIDO IZAR (*Zeitsch. physiol. Chem.*, 1910, **64**, 62—66. Compare Abstr., 1909, ii, 329, 909).—The regeneration of uric acid which occurs in the liver when it is perfused with blood saturated with carbon dioxide is not influenced by small quantities of acids or alkalis (lactic acid, sodium hydroxide), but larger amounts of alkali, and especially of acid, inhibit the phenomenon.
W. D. H.

The Enzymes of the Mammary Gland. W. GRIMMER (*Festschrift Otto Wallach*, 1909, 452—466).—Extracts of the mammary glands of the ox, sheep, goat, pig, and horse contain normally no soluble peroxydase. It is liberated from the cells by destruction of their membrane; it is present when the cells are broken down by purulent disease. The extracts contain very large amounts of catalase, which must be reckoned as an extra-cellular enzyme. The glands of the pig and horse are richest, and that of the ox poorest, in this enzyme. Aldehyde, catalase, reductase, and hydrogenase are absent in all cases, and must be due to bacterial action when they occur in milk. Salolase was found, except in the case of the ox. The salol cleavage is not due to the alkalinity of the medium; salolase is a true enzyme, and is destroyed, by boiling. W. D. H.

The Occurrence of Arginine in the Bull's Testis. GINZABURO TOTANI and K. KATSUYAMA (*Zeitsch. physiol. Chem.*, 1910, **64**, 345—347). —Free arginine has been previously described in ox spleen and fish flesh; it is also present in ox testis. W. D. H.

Lactic Acid Formation in Man. JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1909, xxix—xxxii; *J. Physiol.*, **39**).—Violent muscular exercise increases the lactic acid of the urine, and to a less extent that of the blood; the excess passes off in thirty minutes in the case of the urine, and in forty-five minutes in that of the blood. These results correspond with those of Douglas and Haldane on the changes in alveolar carbon dioxide after exercise. In long-continued exercise, no such marked changes occur. After a Turkish bath, the sweat contains lactic acid, but the amount in the urine is approximately normal. In shortage of oxygen, although the alveolar carbon dioxide is reduced, the lactic acid in the urine does not rise beyond the normal figures.
W. D. H.

Inosite. IV. FRANZ ROSENBERGER (*Zeitsch. physiol. Chem.*, 1910, **64**, 341—344. Compare Abstr., 1908, ii, 873, 1055; 1909, ii, 252).—A continuation of previous work. In the present experiments white mice were used; they were killed, and immediately treated with the

necessary reagents to extract inosite, so that no time elapsed for autolysis to occur; no inosite was found; whether there is one inositogen or several is left open. W. D. H.

The Ionic Concentration in Organic Liquids. I. The Hydrogen and Hydroxyl Ion Concentration in Placental and Retroplacental Serum WALTHER LÖB and SHIGEJI HIGUCHI (*Biochem. Zeitsch.*, 1910, **24**, 92—107).—The method employed was that of concentration cells. The mean hydrogen ion concentration of placental serum freed from carbon dioxide was $p_4 = 7 \cdot 65$ (varying between 0·51 and $0 \cdot 31 \times 10^{-7}$). The hydroxyl concentration varied between 2·3 and $4 \cdot 8 \times 10^{-7}$ (mean 3·13). Results are also given for the retroplacental serum, and the placental serum in cases of eclampsia, in which latter case they differ little from the normal. S. B. S.

Anæroxydase and Catalase of Cow's Milk. J. SARTHOU (*J. Pharm. Chim.*, 1910, [vii], 1, 165—166, 245—247).—Polemical with Bordas and Touplain (Abstr., 1909, ii, 505; this vol., ii, 57), and in support of the views already published (this vol., ii, 57). It is admitted in the second paper that lactoserum, after passage through a Chamberland filter, no longer gives a blue coloration with guaiacol, but this is due to loss of the enzyme. A process for preparing clear lactoserum still containing the enzyme and capable of reacting with guaiacol is described. T. A. H.

Indirect Determination of Bacterial Richness of Cow's Milk. Catalasimetry. J. SARTHOU (*J. Pharm. Chim.*, 1910, [vii], 1, 113—118. Compare this vol., ii, 57).—While the nutritive value of milk is due to its chemical composition, its dietectic value is dependent on its relative freedom from bacteria, and this has usually been roughly measured by the acidity of the milk. The author finds that when 10 c.c. of fresh milk are shaken with 10 c.c. of a solution of hydrogen peroxide, it evolves after ten minutes from 0 to 1·2 c.c. of oxygen, due to the action of the catalase (physiological catalase) naturally present in the milk. On standing in air, milk becomes contaminated with bacteria and develops a further supply of catalase (bacterial catalase), and such milk on treatment with hydrogen peroxide gives an increased yield of oxygen. For ordinary purposes the test may be made with 10 c.c. of milk, but its sensibility is much increased by using 40 c.c. of milk with 10 c.c. of hydrogen peroxide solution.

Tables are given in the original showing the amounts of oxygen disengaged by various fresh and stale milks. T. A. H.

Action of Heat on Milk. ROEMER R. RENSHAW and F. C. WARE (*J. Amer. Chem. Soc.*, 1910, **32**, 391—396).—Richmond (*Analyst*, 1892, **17**, 222) and Richmond and Boseley (*Analyst*, 1893, **18**, 141) have stated that by the action of heat on milk, the specific rotatory power of the lactose is considerably diminished, whilst the reducing power is but slightly decreased.

A study has now been made of this question, and it has been found that a rapid decrease in the amount of sugar takes place on pasteurisa-

tion, but that concordant results are obtained by the optical and gravimetric methods of estimation. It is evident, therefore, that agreement between the results obtained by the two methods cannot be taken, as has been suggested, as indicating that milk has not been pasteurised. In order to ascertain if the decomposition of the lactose is due to the action of the alkaline salts in the milk, a solution containing equivalent proportions of the principal electrolytes found in milk and a quantity of lactose was heated for two and a-half hours at 85°; it was found that, under these conditions, the salts did not have any effect on the sugar. On heating milk between 60° and 85° in presence of a small quantity of formaldehyde, little or no change takes place in the lactose content or acidity. The conclusion is therefore drawn that the decomposition of the lactose is due to certain lactic acid organisms, which act rapidly at 80—85°, and more slowly, but for a longer time, at 60°.

The presence of a sediment containing calcium phosphate in pasteurised milk has been confirmed. E. G.

Does Butter-fat contain Simple or Compound Glycerides? MORITZ SIEGFELD (*Milchw. Zentr.*, 1910, **6**, 122—127).—As the glycerides of the lower fatty acids are soluble in alcohol, it should be possible to extract tributyrin from butter-fat by means of this solvent if the tributyrin were present as a simple glyceride. If butter-fat, however, is treated with alcohol, a small quantity of the fat goes into solution, but the composition of this portion does not differ greatly from that of the original fat. On the other hand, tributyrin can be extracted readily from its mixture with beef-fat. The author is therefore of opinion that butter-fat consists chiefly of compound or mixed glycerides, and that this conclusion also applies to other fats.

W. P. S.

Ionic Equilibrium in the Organism. III. Measurements of the Acidity of Normal Urine. LAWRENCE J. HENDERSON (*Biochem. Zeitsch.*, 1910, **24**, 40—44).—The measurements were carried out by the indicator method of Salm, using neutral-red and *p*-nitrophenol as indicators. In fifty cases the acidity varied between the hydrogen ion concentration of $0{\cdot}4.10^{-7}$ and that of 40.10^{-7}. The mean found was 10.10^{-7}, and the geometrical mean, 5.10^{-7}. S. B. S.

The Iron of the Urine. I. The Estimation of Iron in Urine. OTTO WOLTER (*Biochem. Zeitsch.*, 1910, **24**, 108—124).—The author distinguishes between the loosely-bound iron, which can be separated by boiling the urine with ammonium sulphide, and the more firmly-bound iron, which can be determined only after destruction of the organic matter. The amount of loosely-bound iron was determined in various animals. It is larger in herbivorous than in carnivorous animals. It is practically absent in man. In the case of human urine, the iron is in the form of a colloidal compound which cannot be separated by dialysis. S. B. S.

The Iron of the Urine. II. The Quantity of Iron in Urine OTTO WOLTER (*Biochem. Zeitsch.*, 1910, **24**, 125—145).—The normal

amount of total iron in the urine of a dog of ·20 kilos. is about 1 mg. for twenty-four hours. It varies according to the quality of the diet, being larger after diets containing meat and blood. In man, the normal amount is about 1 mg. for twenty-four hours on a mixed, blood-free diet. In certain pathological cases, iron in loose combination is found in human urine. In these cases the total iron may also be more than normal. In the case of sheep and rabbits, the iron of the urine is increased after ingestion of green fodder. Certain therapeutic preparations can in the case of dog and man cause an increased iron output after continued doses *per os*. Small subcutaneous injections of quite small doses of the officinal iron preparations can cause, both in animals and man, an increased iron output in the urine after a very short interval. S. B. S.

Creatine Excretion in Birds. D. NOEL PATON (*J. Physiol.*, 1910, **39**, 485—504).—In the urine of goose, duck, and hen, creatine takes the place of the creatinine of mammalian urine. Its amount there is a measure of muscle catabolised. In fasting, it increases absolutely, and proportionally to the total nitrogen. Its excretion varies directly, but not proportionately to the total nitrogen. If the "flesh" katabolised during fasting as calculated from the total nitrogen is greater than the "flesh" calculated from creatine nitrogen, non-muscle protein is being utilised. But if the reverse obtains, some of the muscle nitrogen must be retained in the body either by resynthesis in the muscles or in other organs. In well-nourished birds, and during the first day of the fast, non-muscle "flesh" is katabolised. In poorly-nourished birds, and later in the fast, muscle "flesh" is chiefly katabolised and some of the nitrogen is retained. The administration of dextrose has no specific action on the excretion of creatine. W. D. H.

The Quantity of Glycuronic Acid Excreted in Normal and Pathological Human Urine. CARL TOLLENS and F. STERN (*Zeitsch. physiol. Chem.*, 1910, **64**, 39—46).—Estimations were made by the method previously described (Tollens, Abstr., 1909, ii, 836). The daily average for normal urine is 0·37 gram of glycuronic acid. The amount is increased by the administration of sodium salicylate and chloral hydrate, and in poisoning by cresol. W. D. H.

A Red Pigment in Urine. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, **64**, 110—119).—On the addition of hydrochloric acid and formaldehyde to urine, a precipitate is formed which is a combination of formaldehyde and urea. This was first shown by Goldschmidt, and confirmed by May. The material is very insoluble, and some further details are given of its properties; the main new point, however, is that a coloured substance is also precipitated; the intensity of the colour varies in different urines, but the red pigment or its chromogen appears to be always present; its identity is not yet established. W. D. H.

The Amount of Iron in the Organs in Cases of Pernicious Anæmia. JOHN H. RYFFEL (*J. Path. Bact.*, 1910, **14**, 411—413).—Iron was estimated in the ash of organs which were cut into thin

slices and washed until free from hæmoglobin. Previous observers give the normal percentage of iron in the liver as 0·08 to 0·09; in spleen, 0·09 to 0·18, and in kidney, 0·004. In cases of non-hæmolytic anæmia, the figures obtained have been lower than these. All the present eight cases of pernicious anæmia, with one exception, give figures which are much larger. W. D. H.

Phloridzin Diabetes. II. A. ERLANDSEN (*Biochem. Zeitsch.*, 1910, **24**, 1—13. Compare this vol., ii, 146).—The investigations were undertaken with the object of amplifying the experiments of Bang, who ascribed phloridzin diabetes to the increased capacity of the kidneys for eliminating sugar from the blood. The effect of the combined action of adrenaline, which causes an increased sugar production, and of phloridzin was investigated. The preliminary experiments with adrenaline alone indicated that this substance caused a degradation of the glycogen in the liver, with resulting hyperglycæmia. This result was arrived at by determining the amount of sugar in the urine, and the rate of its excretion. Rabbits in summer, when the liver contains less glycogen, excrete less sugar under the influence of adrenaline than animals in spring, when the liver contains relatively large amounts of the complex carbohydrate. It was found that when adrenaline glycosuria is superimposed on phloridzin glycosuria, the total amount of sugar excreted was greater than that due to either drug acting by itself, and that the excretion extends over a longer period. The results are taken to confirm the author's hypotheses as to the nature of phloridzin diabetes. S. B. S.

Gout. HEINRICH BECHHOLD and J. ZIEGLER (*Biochem. Zeitsch.*, 1910, **24**, 146—151. Compare Abstr., 1909, ii, 916).—The authors confirm their previous statement that the uric acid exists in the form of sodium urate in serum, and reply to the criticisms of Gudzent (this vol., ii, 146) on their previous paper. S. B. S.

Œdema as a Colloido-chemical Problem, and Observations on the Nature of Water-fixation in the Organism. MARTIN H. FISCHER (*Kolloidchem. Beihefte*, 1910, **1**, 93—118).—Experiments are described which show that the development of the various forms of œdema is due to changes in the capacity of the tissue for taking up water, and not to an alteration in blood pressure or in permeability of the walls of the blood-vessels. The amount of water which a tissue can take up is determined by the colloids which it contains, and the factors which influence the amount of this absorption appear to be the same for various organic tissues as for emulsion colloids like fibrin and gelatin. In both cases the influence of acids and neutral salts on the swelling properties is of the same character.

The author considers that œdema is the result of an abnormal increase in the swelling capacity of the colloids of the tissue as a consequence of the non-removal of substances which behave like acids in giving rise to a very large amount of swelling. In support of this view it is found that œdema is always accompanied by the formation and accumulation of substances of acid character, and that its

development is hindered by the same substances (salts), which tend to inhibit the swelling of colloids by acids. H. M. D.

Chemical Analysis of a Bone from a Case of Human Adolescent Osteomalacia. FRANCIS H. MCCRUDDEN (*J. Biol. Chem.*, 1910, **7**, 199—200).—The result obtained confirms what was previously noted in osteomalacia in the horse. The quantity of magnesium and sulphur is increased out of all proportions to decrease in the amount of calcium. W. D. H.

The Action of Antimony Compounds in Trypanosomiasis in Rats. JOHN D. THOMSON and ARTHUR R. CUSHNY (*Proc. Roy. Soc*, 1910, *B*, **82**, 249—255).—Various antimony compounds, like those of arsenic, are fatal to trypanosomes. The best combinations of the former metal were combinations with organic acids, corresponding with tartar emetic. The lactate, citrate, malate, and mucate were employed. The last named produced so much local irritation that it was abandoned. The citrate is inferior to the malate and tartrate, which are about equal. The best results, however, were obtained with ethyl antimonyl tartrate. It was tried alone and in combination with atoxyl. There were fewer recurrences when the two drugs were used, but the mortality from poisoning was higher, so that only two rats survived for two months as against six of those treated by the antimony compound alone. Possibly more accurate adjustment of the quantities of the two drugs might combine the advantages of each.
W. D. H.

Action of Neutral Salts in Physiological Processes. RUDOLF HÖBER (*Zeitsch. physikal. Chem.*, 1910, **70**, 134—145).—A summary is given of the order of activity of a number of cations and anions in influencing certain physiological processes, such as hæmolysis, the irritability of muscle, and the movements of ciliated epithelium. Most of the data has already been published (compare Höber, Abstr., 1905, ii, 270; 1908, ii, 28, 121). The order of efficiency of cations in diminishing the amount of work done in ciliary movements of the epithelium from the mouth of the frog is as follows:

$$Li > Cs > Na > Rb > K,$$

and for the anions, I, $Br > NO_3 > Cl$, SO_4. The results of the latter investigation will be published in detail later.

The order of the physiological activity of neutral salts is compared with their influence on certain physico-chemical processes, such as the acceleration of ester hydrolysis, the retardation of protein precipitation in acid and in alkaline solution, the diminution of solubility, and the increase of viscosity. The tabulated data show as regards the anions that the order is substantially the same for physiological and physico-chemical processes, but that in some cases the order is the converse to the usual one. In comparatively few cases is there agreement between the physiological and physico-chemical order of the cations; the most striking agreement with the physiological order is in the precipitation of proteins in neutral solution. In both cases the position of cæsium is abnormal, inasmuch as it takes its place with sodium and lithium

instead of with potassium and rubidium. The effect of the acidity or alkalinity of the solution on the order of activity of the ions, more particularly in colloidal solutions, has already been considered.

G. S.

Rate of Action of Drugs (Alcohol, Chloroform, Quinine, Aconitine) on Muscle as a Function of Temperature. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. Roy. Soc.*, 1910, *B*, **82**, 205—217; *Proc. Physiol. Soc.*, 1909, xxxvi).—The authors find that the effect of the drug can in all the cases examined be expressed by Esson's formula: $\log L_0 - \log L_1 = m(\log T_1 - \log T_0)$, where L_0 and L_1 are the lengths of time required for the abolition of contractility under the influence of the drug at the lower and higher temperatures, and T_0 and T_1 the respective absolute temperatures. Working at several temperatures between 7° and 25°, the values of m obtained were: for ethyl alcohol 20·8 (which corresponds closely with the value, 20·38, observed by Harcourt and Esson for the reaction between hydrogen peroxide and hydrogen iodide), for chloroform 14·3, and for quinine hydrochloride 26·7, the coefficient of increase for 10° being 2·04, 1·63, and 2·52 respectively. In the case of aconitine the toxic effect of solutions $N/10,000$, and even of $N/2000$ and $N/1000$, was completely suspended at 7° to 8°, but made its appearance as soon as the temperature was raised.

The relative toxicities of the four substances on the molecular scale were found to be: alcohol = 1, chloroform = 100, quinine = 2000, aconitine = 20,000.

E. J. R.

Action of Strychnine and Brucine on Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1909, xxvii—xxix; *J. Physiol.*, **39**).—In affinity, brucine is the stronger of the two nux vomica alkaloids. Tested with muscles, strychnine abolishes the contraction more rapidly than brucine, but the recovery from strychnine is more complete and regular. The strychnine effect is the more intense, but the chemical action of brucine is the more fixed and profound. The officinal doses of quinine and strychnine indicate roughly their pharmacodynamic activity, which is in the inverse order to their action on isolated frog's muscle. So far as this tissue is concerned, the relative toxicity of four alkaloids is aconitine 1000, quinine 100, strychnine 12, and brucine 4.

W. D. H.

Action of Poisons on an Enzymatic Process. KARL G. SANTESSON (*Skand. Archiv. Physiol.*, 1909, **23**, 99—142).—Continuing the experiments formerly described (Abstr., 1908, ii, 1061), the influence of a number of salts on the catalytic decomposition of hydrogen peroxide by muscle extract has been investigated. In decinormal solutions all the salts examined, with the exception of sodium sulphate, hinder the process. Potassium, sodium and ammonium sulphates at a concentration of $N/100$ or $N/1000$, as well as potassium carbonate in $N/1000$ solution, accelerate the decomposition. All the other salts investigated hinder the action. Potassium cyanide, potassium, sodium and ammonium nitrates, and potassium chlorate are especially poisonous; potassium bromate, potassium

bromide, sodium chloride, and ammonium chloride are less so, whilst potassium carbonate, potassium chloride, and sodium phosphate exert only a feeble influence on the process. R. V. S.

Chemistry of Vegetable Physiology and Agriculture.

Comparison of Photochemical and Abiotic Action of Ultra-Violet Light. Mlle. P. Cernovodeanu and Victor Henri (*Compt. rend.*, 1910, **150**, 549—551).—A comparison is made in tabular form between the bactericidal action of ultra-violet light of different wave-lengths and the chemical activity of the same rays. The rate of bactericidal action for the rays having γ 2224—4000 Ångström units is a thousand times greater than for rays of λ 3022—4000 units. The ratio between the rates of chemical action for the same rays varies from 1 : 5 to 1 : 16, according to the particular reaction studied. Rays of smaller wave-length than 2800—2900 are destructive to living organisms, and this is precisely the limit below which solar rays undergo complete absorption in the terrestrial atmosphere. W. O. W.

Relation between Penetrative and Bactericidal Power of Ultra-Violet Light and the Chemical Constitution of the Media. Gabriel Vallet (*Compt. rend.*, 1910, **150**, 632—634).—An account of experiments undertaken to ascertain the extent to which the germicidal action of ultra-violet light is inhibited by absorption in the medium. Cultures of *Bacillus coli*, for example, in water, alcohol, glycerol, and many salt solutions are easily sterilised, whilst olive oil, acetic acid, and albumin in 1% solution protect bacteria from the action of the light. A solution containing peptone, dextrose, and potassium hydrogen tartrate resisted sterilisation, although each of the substances singly was transparent to the rays when in solutions of the same concentration. W. O. W.

Bactericidal Properties of Lecithins and Choline Salts. Roemer R. Renshaw and K. N. Atkins (*J. Amer. Chem. Soc.*, 1910, **32**, 130—132).—In view of the contradictory statements which have been made with reference to the bactericidal properties of lecithins, an investigation has been carried out in order to ascertain the influence of these substances on the growth of some of the more common organisms. As it is possible that the presence of choline, a decomposition product of the lecithins, may have caused the divergence of opinion, the bactericidal properties of the hydrochloride and phosphate of this compound have also been studied. The results show that, in general, lecithins cause a varying retardation in the development of bacteria, but that their bactericidal properties are

so slight as to be negligible for practical purposes. In the case of the choline salts, an effect was less frequently observed, and a diminution in the rate of development of the bacteria was less marked.

E. G.

Biochemistry of Micro-organisms. II. The Fermentation of Formic Acid with Bacillus prodigiosus. HARTWIG FRANZEN and G. GREVE (*Zeitsch. physiol. Chem.*, 1910, **64**, 169—261).—A long series of experiments, given with full details, on the action of *Bacillus prodigiosus* in relation to formic acid. These were conducted quantitatively under varying conditions of temperature, concentration, the formate employed, and so forth. The *B. prodigiosus Kràl* is not so energetic either in the formation or destruction of formic acid as is the *B. prodigiosus K.G.-A.* (Kaiserliches Gesundheits-Amt).

W. D. H.

Differences in Denitrification in Soils and in Liquids. ALFRED KOCH and H. PETTIT (*Centr. Bakt. Par.*, 1910, ii, **26**, 335—345).—The results of experiments with arable soil showed that very little, if any, nitrogen is liberated when moderate amounts of nitrate and dextrose are added and the percentage of water is not high.

Further experiments, in which sterilised soils, to which nitrate and different amounts of dextrose were added, were inoculated with *Bacillus fluorescens liquefaciens*, *B. pyocyaneus*, and *Bacterium Hartlebi*, showed that, whilst the decomposition of the nitrate increases with the amount of dextrose present, loss of nitrogen in the free state is inconsiderable when the water in the soil is 18%, unless the amount of sugar is large. The liberation of free nitrogen is, however, considerable when the percentage of water is raised to 25 or 30%. In glass-sand containing 14% of water, there is also a considerable loss of free nitrogen.

As the organisms employed have been shown to liberate over 80% of nitrogen in liquid cultures, owing, perhaps, to less efficient aeration, it is unsafe to assume that the behaviour of soil bacteria is the same in soils as in water. The changes produced by soil organisms should therefore be investigated in soil cultures which involve no special difficulties, except, perhaps, when ammonia has to be determined.

N. H. J. M.

The Influence of an Electric Current on the Assimilation of Carbon Dioxide by Water Plants. A. KOLTONSKI (*Bied. Zentr.*, 1910, **39**, 105—106; from *Beiheft. Bot. Zentr.*, 1908, **23**, i, 204—271).—The author confirms the result obtained earlier by Thouvenin and Pollacci, that the passage of a feeble electric current through the plant increases assimilation; if the current acts for too long, however, injury sets in, and finally death. The direction of the current is also of importance, a current going from the bottom to the top of the stem causing a greater increase than one passing downwards. A current passing through the liquid also stimulates assimilation for a time, but afterwards decreases it.

E. J. R.

Assimilation of Pentoses and Pentitols by Plants. THOMAS BOKORNY (*Chem. Zeit.*, 1910, **34**, 220—221).—The question is raised whether pentoses can, like hexoses, be assimilated by the higher plants or lower organisms, and a certain amount of evidence is adduced to show that they can. Thus xylose and arabinose served as nutrient to yeast and also to bacteria. Experiments of previous workers are quoted to show that the higher plants have no power of utilising xylose; the pentitol and adonitol can, however, be utilised by *Adonis vernalis*. E. J. R.

Development of a Bulbous Plant. Variations in Weight of the Dried Plant. GUSTAVE ANDRÉ (*Compt. rend.*, 1910, **150**, 545—547).—This paper contains in tabular form results of determinations of water, ash, and dry organic matter in onions at different stages of development. The results are discussed and a comparison made between the composition of the bulb and that of the parts above ground at different stages of the plant's growth. W. O. W.

The Photochemical Formation of Formaldehyde in Green Plants. SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1910, *B*, **82**, 226—232).—When grass was washed with warm water no formaldehyde could usually be detected in the washings; if, however, the grass was extracted with methylated spirit, the extracts on evaporation and treatment with ether gave a solution which almost always contained formaldehyde. It is argued that chlorophyll contains the aldehyde in a state of stable combination.

The photochemical formation of formaldehyde by chlorophyll was confirmed; 1 c.c. of an ethereal solution of chlorophyll was allowed to evaporate at room temperature on a strip of glass 140×20 mm. Some films thus prepared were kept in the dark, others were exposed to moist carbon dioxide in sunlight, others to sunlight over lime or soda-lime, and others, again, were exposed to moist carbon dioxide in the dark. No formaldehyde was formed in the dark, very minute quantities were detected on the films kept in sunlight over lime or soda-lime, whilst a distinct reaction was obtained from films kept in sunlight over moist carbon dioxide.

In attempting to explain the non-accumulation of formaldehyde in the plant-cell, the author supposes that the reaction is similar to one studied by Schiff:

$$CO_2H\cdot CHR\cdot NH_2 + HCHO \rightleftharpoons CO_2H\cdot CHR\cdot N{:}CH_2 + H_2O,$$

and may be represented thus:

$$\text{chlor}{<}^{H}_{H} + HCHO \rightleftharpoons \text{chlor}{<}{>}CH_2 + H_2O,$$

The condensation product being somewhat stable, equilibrium will be maintained when only a very small amount of free aldehyde is present; as this is removed by synthesis into sugars, etc., more of the condensation product will decompose. In presence of sunlight and carbon dioxide there is probably a continuous synthesis of formaldehyde and a continuous condensation of the latter to sugars without at any time such an accumulation of aldehyde as to be toxic to the cell.

A modified and much more sensitive form of Rimini's test was used. To 10 c.c. of the liquid to be tested, add 2 c.c. of a 1 per cent. solution of phenylhydrazine hydrochloride freshly made up and filtered, and then 1 c.c. of a fresh 5 per cent. solution of potassium ferricyanide and, finally, 5 c.c. of hydrochloric acid. A brilliant, magenta-like colour develops if formaldehyde is present, the intensity of which gives an indication of the actual quantity within certain limits (1 in 1,000,000 and 1 in 100,000). In testing for polymeric forms (oxymethylene or combinations like hexamethylenetetramine) it is necessary to allow the mixture to remain for some hours or to warm it for a short time after adding the phenylhydrazine hydrochloride and before adding the ferricyanide and the hydrochloric acid. Acetaldehyde gives no reaction, and furfuraldehyde a transient, dirty green colour.

E. J. R.

The Action of Gaseous Formaldehyde on Green Plants. VIKTOR GRAFE and LEOPOLD R. VON PORTHEIM (*Bied. Zentr.*, 1910, **39**, 140—141; from *Oesterr. bot. Zeitsch.*, 1909, **59**, 19—25, 66—74).—Seedlings of *Phaseolus vulgaris* were grown in pots under bell jars in an atmosphere containing formaldehyde, precautions being taken to keep the soil as free as possble from contamination with this substance. Formaldehyde is not injurious even when present to the extent of 0·04% of the atmosphere; on the contrary, it increases the amount of growth. It somewhat changes the habit of the plant, and is considered to exert a formative stimulus. E. J. R.

Penetration of Inorganic Salts into Living Protoplasm. W. J. V. OSTERHOUT (*Zeitsch. physikal. Chem.*, 1910, **70**, 408—413).—In order to find out whether calcium salts can penetrate into living uninjured cells, seeds were grown on the surface of distilled water until the root hairs were clearly visible, and the cells seen to be free from calcium oxalate. The seeds were then placed in very dilute solutions (0·005 molar) of certain calcium salts, and in one and a-half to four hours crystals of calcium oxalate could be detected inside the cells on examination with crossed nicols. The subsequent growth of the cells showed that they had suffered no injury. The experiments were made at 30°. G. S.

The Influence of Mineral Salts on the Protein Changes in Plants. W. ZALESKI and W. ISRAILSKY (*Biochem. Zeitsch.*, 1910, **24**, 14—21).—The experiments were carried out with the seeds of *Lupinus angustifolius* and *Triticum sativum*, which were softened in distilled water and then grown in various water cultures, control plants being also grown in distilled water. After intervals, the the plants were washed and dried between paper, and the water and protein estimated separately in the axial organs and in the cotyledons or endosperm. Magnesium sulphate inhibits both protein degradation and the formation of protein in the axial organs in the case of lupins, which is in contrast to the stimulating action on protein metabolism of other salts, such as calcium nitrate. In the case of wheat embryos, the authors ascribe a stimulating action to nitrates, the nature of which they discuss. S. B. S.

Stimulation of Premature Ripening by Chemical Means. ALBERT E. VINSON (*J. Amer. Chem. Soc.*, 1910, **32**, 208—212).—A study has been made of the influence of more than one hundred substances in effecting the premature ripening of dates. It has been found that, in general, the efficiency of a substance is more or less proportional to its volatility; thus, for example, benzene and toluene act very completely during one night, whilst xylene is much less active, and camphor and naphthalene are not volatile enough to produce any effect. From a consideration of these results and the author's work on the invertase of the date (Abstr., 1908, ii, 724), the conclusion is reached that any substance which can penetrate the cuticle and kill or stimulate the protoplasm, thereby liberating the previously insoluble intracellular enzymes without rendering them inactive, will bring about ripening, provided that the fruits have already attained a certain degree of maturity. A study of the action of heat on the fruits has shown that if dates are heated sufficiently to destroy protoplasm but not enzymes, the ripening will proceed to completion, whilst at higher temperatures all ripening ceases. E. G.

Presence of Stachyose in the Underground Parts of Labiate Plants. L. PIAULT (*J. Pharm. Chim.*, 1910, [vii], 1, 248—255).—This sugar has been found already in the underground parts of *Lamium album* (Abstr., 1909, ii, 338). As the result of preliminary experiments on the action of invertase on extracts of a number of Labiate plants, the author examined *Stachys lanata*, *S. sylvatica*, *S. recta*, *Origanum vulgare*, *Mentha sylvestris*, *Ballota foetida*, *Clinopodium vulgare*, *Salvia splendens*, and *S. pratensis*, and isolated stachyose from each of these plants. The sugar was examined by the determination of melting point, optical rotation, and water of crystallisation in each case. Details of the method of extraction are given. By heating stachyose with 2 per cent. solution of sulphuric acid at 100° in closed tubes, lævulose only is split off in the first ten to twenty minutes. T. A. H.

The Occurrence of Betaine in the Chenopodiaceæ. VLADIMIR STANĚK and K. DOMIN (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 297—304).—The following method of estimating betaine is used: 15—150 grams of the dry powdered substance are extracted with alcohol. The extract is concentrated to about 50 c.c., treated with 1—3 grams of sodium hydroxide (according to the quantity of fat present), and warmed for half an hour to saponify the fats and decompose the lecithin. It is then diluted to 100—200 c.c., heated to boiling, and treated with a 10 per cent. solution of copper chloride drop by drop until the alkaline reaction disappears. Cuprous oxide is first precipitated, then copper hydroxide, and probably also a copper oxychloride that precipitates purine bases and albumins. The filtrate is treated with hydrogen sulphide to remove copper, evaporated to dryness, and taken up with a saturated solution of sodium chloride in 5 per cent. hydrochloric acid; the filtered extract is then treated with potassium tri-iodide. After two hours, the precipitate is filtered, washed with saturated sodium chloride solution, and decomposed with

copper; the filtered solution is neutralised with sodium carbonate, and treated with a solution of iodine in 10 per cent. potassium iodide, which, after six hours, precipitates the chlorine. The filtrate is acidified with 5 per cent. hydrochloric acid, saturated with sodium chloride, and treated with potassium tri-iodide to precipitate betaine. After two hours the precipitate is collected, and changed into betaine chloride by treatment with copper and copper chloride.

Only two plant species appear to contain betaine as a regular constituent: the Chenopodiaceæ and the Amarantaceæ, in other families the occurrence being irregular. The dry matter of the leaves of *Atriplex canescens* contains 3·78 per cent. of betaine, whilst for *Beta Cycla* the corresponding number is 3·36. These values, however, are higher than are given by the majority of the plants examined. E. J. R.

Influence of the Method of Drying on the Composition of Gentian Root. Preparation of Gentiopicrin from the Dry Root. ÉMILE BOURQUELOT and M. BRIDEL (*J. Pharm. Chim.*, 1910, [vii], 1, 156—162).—It had been shown previously that for the isolation of gentiopicrin, ordinary dry gentian root of commerce is unsuitable, and that the fresh root must be used (Abstr., 1900, i, 511; 1902, i, 713, 744). It is now found that if the root is dried by exposure to air or at temperatures up to 35°, no loss of gentiopicrin occurs, and root so prepared can be used for the preparation of the glucoside. The absence of gentiopicrin from commercial dry root is due to the fermentation process to which the latter is subjected. Particulars of the cupric reducing power and optical rotation of extracts prepared from roots dried in various ways are given in the original. T. A. H.

Chemical Examination of Watermelon Seed. FREDERICK B. POWER and ARTHUR H. SALWAY (*J. Amer. Chem. Soc.*, 1910, **32**, 360—374).—The seeds of the watermelon (*Cucurbita citrullus*) consist of shells, 48·7%, and kernels, 51·3%. They do not contain any alkaloid or glucoside.

The kernels, on expression, yielded 7·4% of oil (calculated on the whole seed). The entire seed, on extraction with light petroleum, gave 19·0% of oil. The expressed oil was optically inactive, and furnished the following constants: D_{20}^{20} 0·9233; acid value, 3·9; saponification value, 191·8; iodine value, 121·1. It consisted of the glycerides of linoleic acid (45%), oleic acid (25%), and palmitic and stearic acids (30%), together with a very small quantity of a phytosterol, $C_{20}H_{34}O$, m. p. 163—164°.

The residual cake contained about 6% of oil (calculated on the whole seed), some soluble protein products, sugar, and resinous material. From the resin were isolated a very small amount of a phytosterol, m. p. 158—159°, and an alcohol, termed *cucurbitol*, $C_{24}H_{40}O_4$, m. p. 260°, which yields an *acetyl* derivative, m. p. 150°. Cucurbitol seems to be closely related to grindelol (Abstr., 1908, ii, 526) and ipurganol (Abstr., 1909, i, 819).

The shells yielded an oil which resembled that of the kernels, but

contained a small amount of arachidic acid. From the resinous material obtained from the shells were isolated a phytosterol, m. p. 138—140°, and cucurbitol. The resin both from the kernels and the shells was found to be physiologically inactive. E. G.

Chemical Examination of Ornithogalum thyrsoides. FREDERICK B. POWER and HAROLD ROGERSON (*Pharm. J.*, 1910, [iv], **30**, 326—328).—The investigation was undertaken with a view to isolating the constituent, or constituents, to which the toxic action of this South African plant is due. A number of physiologically inactive substances were isolated in a pure state, and it was ascertained that the toxicity is due to one or more constituents of the resinous portion of the alcoholic extract.

The entire plant was ground and completely extracted with hot alcohol, and the extract so obtained was resolved into (1) a portion volatile in steam and consisting of palmitic acid with a small amount of a yellow volatile oil having a persistent odour; (2) a part soluble in water and containing inorganic salts, a reducing sugar yielding *d*-phenylglucosazone, and indefinite organic matter, and (3) a dark green resin. No alkaloid is present.

The resin was extracted in succession with light petroleum (I), ether (II), chloroform (III), ethyl acetate (IV), and alcohol (V), and these extracts separately examined.

(I) yielded pentatriacontane, a *phytosterol*, $C_{27}H_{46}O$, m. p. 133—134°, $[\alpha]_D$ $-33\cdot6°$, palmitic acid, and small amounts of formic and butyric acids.

(II) furnished ipuranol (Trans., 1908, **93**, 907), $[\alpha]_D$ $-37\cdot2°$ in pyridine (the diacetyl derivative has $[\alpha]_D$ $-25\cdot4°$ in ethyl acetate), a light brown resin sparingly soluble in ether, with a little formic acid and indefinite resinous matter.

(III) consisted mainly of resin, soluble in sodium hydroxide, but not in sodium carbonate solution; on hydrolysis it furnished a small amount of a crystalline substance, m. p. 176—180°, soluble in ether, and a product which reduced Fehling's solution, but yielded no phenylosazone.

(IV) and (V) formed dark resinous masses, from which nothing definite could be isolated. The air-dried plant and the crude resin both proved toxic to guinea-pigs, as did also the various extracts of the resin referred to above, with the exception of (I); the ether extract was the most active. T. A. H.

Chemical Examination of Pumpkin Seed. FREDERICK B. POWER and ARTHUR H. SALWAY (*J. Amer. Chem. Soc.*, 1910, **32**, 346—360).—A study has been made of the composition of the seeds of the common pumpkin (*Cucurbita Pepo*).

The kernels were separated from the shells, and, on expression, yielded 19·3% of oil (calculated on the whole seed). The entire seed, on extraction with light petroleum, gave 34·3% of oil. The expressed oil was optically inactive, and furnished the following constants: D_{20}^{20} 0·9220; acid value, 3·4; saponification value, 189·4; iodine value, 119·7. It consisted of the glycerides of linoleic acid (45%), oleic

acid (25%), and palmitic and stearic acids (30%), together with very small quantities of a phytosterol, $C_{27}H_{46}O$, m. p. 162—163°, and a similar substance of lower m. p.

The residual cake contained 8·7% of oil (calculated on the whole seed), some soluble protein products, sugar, resinous material, and a very small amount of salicylic acid. An *acid*, $C_{25}H_{51}O \cdot CO_2H$, m. p. 99°, was isolated from the resin; its *ethyl* ester has m. p. 61°.

The shells constituted 20·8% of the whole seed, and contained 2·6% of oil (calculated on the whole seed), which resembled that obtained from the kernels.

Pumpkin seeds do not contain any principle of marked physiological activity, and any medicinal value which they may possess must therefore be due to a mechanical effect. E. G.

Existence of Glucosides in Varying Proportions in Two Species of Veronica. J. VINTILESCO (*J. Pharm. Chim.*, 1910, [vii], 1, 162—165).—Bourquelot's method for the detection of glucosides in plants by the use of emulsin (Abstr., 1902, ii, 55) has been applied by the author to *Veronica officinalis* and *V. Chamaedrys*. Both the plants contain a lævorotatory glucoside, which is hydrolysed by emulsin, yielding dextrose as one product. The glucoside exists in greatest proportion during the vegetative period in both plants, and in largest quantity in the first named. Both plants also contain a sugar, which is hydrolysed by invertase, and soluble ferments capable of hydrolysing both the sugar and the glucoside. Powdered veronica of commerce contains soluble ferments, which decompose sucrose, amygdalin, and salicin. T. A. H.

The Influence of Carbon Disulphide on the Decomposition of Nitrogenous Compounds in the Soil. RICHARD SCHERPE (*Bied. Zentr.*, 1910, **39**, 79—87; from *Arb. K. Biol. Aust. Land-Forstw.*, 1909, **7**, 353. Compare Russell and Hutchinson, *J. Agri. Sci.*, 1909, **3**, 111).—The author shows that treatment with carbon disulphide leads to a change in the processes going on in the soil. There is an accumulation of ammonia and nitrates in the partially sterilised soil after some time, but the experiments do not show whether or not nitrification has been suspended. The influence of chalk, straw, humin, etc., was investigated, but no very definite results were obtained. E. J. R.

Organic Nitrogenous Compounds in Peat Soils. S. L. JODIDI (*J. Amer. Chem. Soc.*, 1910, **32**, 396—410).—The analysis of a typical sample of Michigan brown peat has given the following results: C, 55·06; H, 5·21; N, 2·74; S, 0·35; ash, 6·62; O (by difference), 30·02. With the object of ascertaining the effect of atmospheric influences on the peat, a sample of weathered brown peat was also analysed, and gave: C, 54·35; H, 5·56; N, 2·69; S, 0·34; ash, 3·79; O (by difference), 33·27. On repeatedly digesting the peat with acid, about 68% of the total nitrogen was extracted. In the case of each sample, estimations were made of the proportions of this dissolved

nitrogen existing as ammonia, amide-nitrogen, amino-nitrogen, and diamino-nitrogen. The results are tabulated.

Neither of the samples contained any nitrogen in the form of nitrates. The amount of nitrogen present as ammonia varied from 0·005% in the weathered sample to 0·041% in the other sample, these amounts being calculated on the oven-dried peat. From two-thirds to three-quarters of the nitrogen extracted with acid is present in the form of amino-acids, about one quarter in the form of amides, and the remainder as diamino-acids. The organic nitrogenous substances present in the brown peat change but very slowly on weathering.

E. G.

Is the Hygroscopic Nature of "Potash Salts" an Advantage to Vegetation? BRUNO TACKE (*Bied. Zentr.*, 1910, **39**, 98—101; from *Deut. landw. Presse*, **36**, No. 71).—Pot experiments are described in which "muriate of potash," "40 per cent. potash salts," kainite, and carnallite are used as manurial dressings. It is shown that the presence of these potassium compounds somewhat hinders the movement of water from the soil to the plant.

E. J. R.

Manurial Action of Nitrates and Nitrites. OSKAR KELLNER (*Landw. Versuchs-Stat.*, 1910, **72**, 311—317).—Pot experiments in which oats were grown in soil (6 kilos.) with 0·5 gram of nitrogen as nitrates and nitrites respectively, and with 0·25 gram in the same forms.

The results showed that even with the smaller amount of nitrite, growth was retarded and the leaves remained rolled up. Later, the plants gradually recovered, and the final growth was equal to that of the plants supplied with nitrates. The larger amount of nitrite, corresponding with 166 kilos. per. hectare, was injurious to germination, but not when applied later.

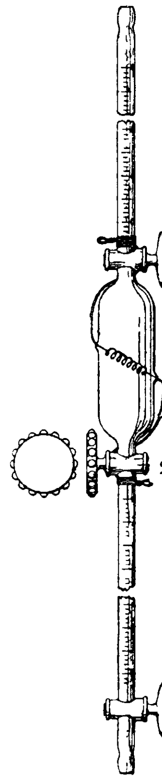
In practice it is of importance to avoid any check in the development of the young plants, and it is therefore desirable that calcium nitrate should be obtained with as little nitrite as possible.

N. H. J. M.

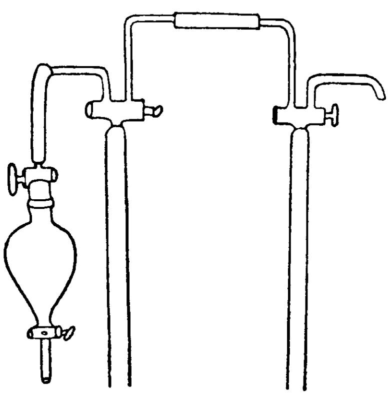
Analytical Chemistry.

New Form of Eudiometer. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1909, 7, 304—308).—This is a simple and convenient form of eudiometer adapted to rapid analysis. Its special feature is that the ordinary levelling tube used to adjust the pressure is not necessary. The instrument shown in the cut is filled with the gas to be exploded while immersed in water contained in a sufficiently deep cylinder. The gas is allowed to enter the instrument while cocks 2 and 3 are open until the level of the water inside has fallen to graduation 6 on

the divided tube between the cocks 2 and 3. Cock 1 is then closed, and the instrument lowered in the water until the reading of the outer water on the upper scale (above cock 1) is the same as the reading of the internal water on the lower scale between cocks 2 and 3. The instrument is then clamped, and cock 2 closed by means of a glass rod; teeth are provided on cock 2 for this purpose. The gas is then exploded and after cooling, cock 2 opened. Water rises in the tube 2 3, and the instrument is then lowered in the outer vessel of water until the reading of external water on the upper scale is the same as that of the internal water in tube 2 3 on the lower scale. The pressure on the products of the explosion is then the same as that under which the original gas volume was measured. If any change of temperature has occurred in the external water, a correction can be introduced by taking into account the alteration of the vapour tension of water. The instrument shown has a capacity of 50 c.c., and the lower tube measuring the contraction, a volume of 6 c.c. graduated in tenths. The upper graduated tube necessarily has the same bore and graduation as the lower one. The instrument is very useful for estimating small proportions of hydrogen, oxygen, or methane in mixtures which on explosion show only a small contraction. Values are given showing that it is trustworthy. W. A. D.



Simplified Form of Eudiometer for General Gas Analysis. Frederic W. Richardson and Adolf Jaffé (*J. Soc. Chem. Ind.*, 1910, **29**, 198—199).—The side-flask with its stoppered thistle funnel and small reflux bulb, or the bulb made from an ordinary pear-shaped separator, is exhausted by means of a Geissler filter pump. By means of the vacuous side-bulb, the estimation of gases dissolved in water is easily carried out. The bulb with the measured volume of water is immersed in water at 80°. The gases are soon extracted and removed to the laboratory vessel. Into this the usual series of absorbents are introduced. If the amount of the gases is very small, a larger amount, say 400 c.c., must be operated on.



The apparatus is very suitable for the estimation of carbon dioxide in baking powders and minerals. The substance can either be weighed in the flask referred to or in a dry pear-shaped 50 c.c. bulb stoppered at both ends; hydrochloric acid is then allowed to enter from the lower end. When using the apparatus for coal gas, a gas-explosion burette is attached to the side outlet from the laboratory tube. The usual absorbents are used. The scum on the surface of the mercury due to the action of bromine, which interferes with the reading, may be removed by means of potassium cyanide. L. DE K.

[Analysis of Gases by means of their Refractive Powers.] LUDWIG STUCKERT (*Zeitsch. Elektrochem.*, 1910, **16**, 37—75).—See this vol., ii, 245.

Some New Forms of Apparatus for the Analysis of Blood Gases by the Chemical Method. THOMAS GREGOR BRODIE (*J. Physiol.*, 1910, **39**, 391—396).—Various modifications introduced to secure accuracy and saving of time are described in the Barcroft-Haldane apparatus. Pipettes for collecting the blood and for delivering it into the analysis bottle, and a new form of water-bath are also described. W. D. H.

Improvements in the Technique of Blood-gas Analysis. JOSEPH BARCROFT and FF. ROBERTS (*J. Physiol.*, 1910, **39**, 429—437). —Modifications in the Barcroft-Haldane apparatus and in the mercury pump are described. The delicacy of the differential apparatus can be increased to serve for analyses of 0·1 c.c. of blood. W. D. H.

[Physico-chemical Volumetric Analysis. Precipitation and Measurement of Electrical Conductivity.] PAUL DUTOIT (*J. Chim. Phys.*, 1910, **8**, 12—26).—A method of volumetric analysis is described, which is based upon the determination of the end-point in a precipitation process by means of conductivity measurements. If, for instance, successive quantities of a concentrated solution of an iodide are added to a dilute solution of a silver salt, and the conductivity of the solution after each addition is plotted as a function of the volume of added iodide solution, two approximately straight line curves are obtained, which intersect at a point corresponding with the complete precipitation of the silver from the solution. An examination of the factors which influence the sharpness of the determination indicates that the solution to be analysed should be as dilute, and the added reagent as concentrated, as possible. Foreign substances which take no part in the precipitation reaction have no appreciable influence on the sharpness with which the end-point can be determined. In cases in which the precipitated substances are only moderately insoluble, the point of intersection of the two curves is more accurately obtained by extrapolation from measurements of the conductivity of solutions containing appreciably more and appreciably less of the added reagent than that corresponding with the end-point. To obtain accurate results, the temperature of the measured solution must be

kept constant to $\pm 0{\cdot}1°$. A special form of capillary burette is described, by means of which the added quantities of reagent solution can be determined to about 0·001 c.c. H. M. D.

Physico-chemical Volumetric Analysis. II. Estimation and Separation of the Alkaline-earth Metals. PAUL DUTOIT and PIERRE MOJOÏU (*J. Chim. Phys.*, 1910, **8**, 27—41. Compare preceding abstract).—The conductivity method of analysis described in the previous paper has been examined for the case of the alkaline-earth metals. It is found that the method can be applied in the estimation of calcium by precipitation as oxalate, sulphate, and carbonate; of strontium by precipitation as chromate, sulphate, carbonate, and oxalate, and of barium by precipitation as sulphate, chromate, silicofluoride, and carbonate. The method can also be used for the estimation of calcium, strontium, and barium when all there are present in a given solution. This estimation necessitates three series of titrations and conductivity measurements with separate portions of the solution. To the first portion, two volumes of ethyl alcohol are added, and this solution is then titrated with a solution of lithium sulphate. The conductivity measurements of this series give Ba + Sr + Ca.

One volume of alcohol is added to the second portion, and this is titrated with a solution of lithium chromate. The conductivity curves of this series give Ba + Sr. To the third portion one volume of alcohol is added, and the solution titrated with cupric silicofluoride. The curves for this series give Ba.

By experiments with solutions of chlorides of the metals, it is shown that this method of analysis gives satisfactory results provided none of them is present in relatively very small quantity.

H. M. D.

The New Heraeus Platinum Crucible Lid. ALEXANDER GUTBIER (*Chem. Zeit.*, 1910, **34**, 211).—This lid, which is laid loosely on the crucible, has several perforations and also a partition wall penetrating half way into the crucible. The right side only of the bottom of the crucible is heated with a small Bunsen (so-called micro) burner, and the flame, which is gradually enlarged, is at first kept at a distance of 3—4 cm. This arrangement causes a circulation of air through the interior of the crucible, and consequently a more rapid combustion of the organic matters, whilst formation of black cinder is prevented. L. DE K.

Collection of Small Precipitates. EMIL DIEPOLDER (*Chem. Zeit.*, 1910, **34**, 176).—A conical flask into which the filtrate is received is fitted with a doubly perforated cork. Through one of the holes passes a funnel, and through the other a tube bent at a right angle and connected to a suction apparatus. In the stem of the funnel is suspended a glass rod, the top of which has the form of a disk, and is made by pressing the end of the rod, whilst red-hot, on an asbestos board. On to the disk is then placed a disk of filter-paper 7 mm. in diameter to retain the precipitate. L. DE K.

Modified Chlorine Absorption Apparatus. R. H. McCrea (*Chem. News*, 1910, **101**, 77).—The solution of iodide is placed in an inverted retort as usual, but a small distilling flask is used to distil from. On the neck of this is placed a piece of india-rubber tubing doubled on itself, which is then thick enough to close loosely the mouth of the retort. H. M. D.

Test for Ozone in Flames. Wilhelm Manchot (*Ber.*, 1910, **43**, 750—751).—In the author's method for proving the presence of ozone in flames (Abstr., 1909, ii, 993), silver may be replaced by either mercury or lead, although the best results are obtained with the first two metals. The best results are obtained when the flame (oxy-hydrogen or hydrogen) is long and narrow, and the surface of the metal should then become coated with intense dark blue patches.

In the latter part of the paper it is pointed out that Loew's claim for priority (Abstr., 1909, ii, 993) does not affect the author's experiments. T. S. P.

Control of the Quantity of Sulphurous Acid Utilised in Sulphitation Processes. G. Fouquet (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 763—771).—The quantity of sulphurous acid present in various forms in a liquid may be estimated by titrating the alkalinity of the liquid, using litmus paper as indicator, and also titrating the liquid with iodine solution. The latter titration gives the total quantity of sulphurous compounds, whilst from this, combined with the former, the amount present as "bisulphite" can be deduced. Soluble hydrogen sulphites are neutral to litmus paper, whilst normal sulphites exhibit a titre corresponding with 1/3CaO per gram of SO_2. For example: one gram of SO_2 introduced into an alkaline solution, and forming normal sulphite alone, diminished the alkalinity towards litmus, expressed as CaO, in the proportion of $7/8 - 1/3 = 13/24$, or if converted into the hydrogen sulphite, the decrease in alkalinity amounted to 7/16, expressed as CaO. Formulæ are given for calculating the sulphurous compounds present in a liquid, the above facts being taken into account. W. P. S.

A Practical Gas Generating Arrangement in Connexion with the Nitrometer. Erwin Rupp (*Chem. Zeit.*, 1910, **34**, 268).—The arrangement consists of a nearly rectangularly bent glass tube 2—3 cm. wide, with short closed ends, and fitted with a tubulus provided with a rubber cork and a connecting tube.

In one of the limbs is placed the solution to be tested, and in the other the reagent. By inclining through 45°, the two liquids are made to mix. L. de K.

Detection of Nitrates in Presence of Bromides, Iodides, and Ammonium Compounds. Sven Goldschmidt (*Chem. Zeit.*, 1910, **34**, 267—268).—Should the solution contain no iodide, sulphite, or thiosulphate, a little potassium iodide is added. Excess of sulphuric acid is added, and the gases evolved are blown through two tubes containing aqueous sodium hydroxide, and then through a solution of potassium iodide and starch. If nitrates are present, the nitric peroxide evolved turns the liquid blue.

Chlorates may be decomposed by heating with hydrochloric acid before applying the test. L. DE K.

[Indirect] Iodometric Estimation of Phosphoric Acid and of Magnesium in the Triple Phosphate. R. BRANDIS (*Zeitsch. anal. Chem.*, 1910, **49**, 152—157).—The process is based on the decomposition of ammonia by hypobromite. The triple phosphate obtained as usual is freed from adhering ammonia by washing with 95% alcohol, which is then in turn removed by means of ether. The ether having evaporated, the precipitate is dissolved in as little as possible 4*N*-sulphuric acid, and the solution is rendered faintly alkaline with 2*N*-sodium hydroxide. Fifty c.c. of alkaline hypobromite solution of known strength are added, followed by 2—3 grams of potassium iodide and 15—20 c.c. of 4*N*-sulphuric acid. The iodine liberated is then titrated with standard thiosulphate. The difference in c.c. of thiosulphate between the titration and the check on the bromine solution represents the phosphoric acid or magnesia respectively. L. DE K.

Estimation of Phosphates by Direct Titration. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 775—777) — The process described previously by the author (Abstr., 1909, ii, 759) can only be applied to ammonium phosphate after the ammonia has been removed by boiling the salt with an alkali. Phenolphthalein and helianthin are the only indicators which can be used, other indicators having been found by experiment to give indistinct end-points in the titration; the method cannot be used in the case of phosphates of the alkaline earths. W. P. S.

Estimation of Boric Acid in Complex Mixtures, and Especially in Plant Ashes. GABRIEL BERTRAND and H. AGULHON (*Bull. Soc. chim.*, 1910, [iv], **7**, 125—130; *Ann. Chim. anal.*, 1910, **15**, 89—93. Compare this vol., ii, 241; Copaux and Boiteau, Abstr., 1909, ii, 345).—The method used is stated to be suitable for the estimation of small quantities of boric acid. It depends on the conversion of boric acid into methyl borate, and the titration of this by a slight modification of Thomson's process (Abstr., 1894, ii, 28) with the application of Jones' method (Abstr., 1899, ii, 332; 1900, ii, 47). Full working details and a sketch of the apparatus are given in the original. T. A. H.

Titrimetric Estimation of Carbon Dioxide. ALBERT VESTERBERG (*Zeitsch. physikal. Chem.*, 1910, **70**, 551—568).—Winkler's method of estimating mixed solutions of alkali carbonate and hydroxide, according to which excess of barium chloride is added and the alkali titrated with dilute acid and phenolphthalein, is applied to the estimation of carbon dioxide in a number of modes of occurrence. Winkler's method has been shown to be very accurate by Küster (compare Abstr., 1897, ii, 74).

For estimating carbon dioxide in distilled water, 250 c.c. of the sample are placed in an Erlenmeyer flask, 25 c.c. of barium chloride

solution (100 grams of the crystallised salt per litre) and 10 c.c. of barium hydroxide are added, the mixture left for some time until the barium carbonate has become granular, and then titrated with hydrochloric acid and phenolphthalein. The accuracy of the method has been proved by decomposing known amounts of sodium carbonate with excess of acid, absorbing the carbon dioxide in barium hydroxide solution containing the chloride, and titrating with hydrochloric acid.

In one form of apparatus used for decomposing carbonates, the usual flask and dropping funnel arrangement is attached to a vessel containing the solution of barium chloride, and which is evacuated by a filter pump and then closed before the experiment is commenced. The advantages of this method, which is particularly useful when the amount of carbon dioxide is large, are that the gas comes off under diminished pressure, and also that there is no danger of incomplete absorption.

The titration of carbonic acid in natural waters by the above method is disturbed by the precipitation of magnesium hydroxide, but better results are obtained when sucrose (10 grams) is previously added. By this method the magnesium appears to be retained in solution. In this and the other methods, the titration is only carried out after the carbonate has become granular.

The error in the ordinary method of estimating the hardness of water by boiling caused by the solubility of calcium carbonate can be overcome by boiling with excess of calcium chloride, which secures the complete precipitation of both the calcium and magnesium as carbonates. The precipitate is then dissolved in acid, boiled to get rid of carbon dioxide, and the excess of acid determined with alkali by titration. G. S.

Estimation of Silicon in High-Grade Ferrosilicon. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1910, 23, 301).—Instead of fusing the sample with potassium sodium carbonate and sodium peroxide in a platinum crucible, the author proceeds as follows:

0·5 Gram of the finely-powdered sample of ferrosilicon or silicon carbide is fused in a covered nickel crucible of 100 c.c. capacity with 10 grams of potassium hydroxide free from silica, first at a moderate heat for twenty minutes, and then at a stronger heat for the same time. The fused mass is allowed to cool, treated with hot water, and the solution is then transferred to a dish. The silica is then separated in the usual way by evaporating with hydrochloric acid. A second evaporation is advisable. Ten % ferrosilicon may be decomposed by heating 0·5 gram of the powder with 10 grams of potassium chlorate and 100 c.c. of hydrochloric acid, but the silica obtained on evaporation is not quite pure, and must be submitted to the fusion process. L. DE K.

Speedy Detection of Potassium in Small Amounts. L. T. BOWSER (*J. Amer. Chem. Soc.*, 1910, 32, 78—79).—Bray (Abstr., 1909, ii, 431) has studied the reaction for the detection of potassium by sodium cobaltinitrite, and has recorded the conditions under which

the test is most sensitive. It is shown by the present author that if an equal volume of alcohol is added to the reaction mixture, prepared according to Bray's directions, the precipitate appears in a few minutes, instead of several hours. Care must be taken to ensure the removal of ammonium salts before applying the test for potassium, since, in the presence of alcohol, ammonium is precipitated as quickly as potassium. Potassium salts can be detected by means of the reagent when they are present to the extent of two parts per 100,000, and ammonium salts when present to the extent of five parts per 100,000. E. G.

Methods of Analysis of the [Native] Potassium Salts. HERMANN ROEMER (*Chem. News*, 1910, **101**, 54—58).—A full description of the processes for the partial and full analysis of "potash salts" as adopted by the International Congress of Applied Chemistry at Berlin, 1903. No important novel analytical matter is introduced in these methods, so only a few points need be mentioned. It is recommended that the quantity actually taken for analysis shall be such that 1 mg. of the potassium platinichloride, or of the potassium perchlorate obtained in due course, shall represent 0 1% of potassium chloride or 0·1% of potassium sulphate, as desired. The platinichloride should be washed with 96% alcohol, and as it cannot be got into the ideal state, it is as well to retain the old atomic weight of platinum (197·2).

A process is given for the recovery of the platinum from the precipitates and alcoholic washings. These are united and boiled with water, zinc or sodium hydrogen carbonate being added for the reduction. The platinum is washed first with water and then with hydrochloric acid, and finally converted into a 10% solution of platinichloride as usual. Any platinous chloride or nitrous compounds may be oxidised by boiling with hydrogen peroxide.

Water is estimated as follows: 10 grams of the sample (chloride or sulphate) are heated in a weighed covered platinum crucible at a dull red heat for some twenty minutes. When much magnesium chloride is present, a layer of calcium oxide or lead oxide should be sprinkled over the salt. L. DE K.

Analysis of Refined Nitres, Gunpowders, and Explosives Containing Chlorates. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1909, **7**, 403—412).—The methods for detecting and estimating chlorates already described (Abstr., 1909, ii, 179, 433, 753) can be applied as follows to nitres and explosives.

Nitres: *Qualitative.*—Add 3 c.c. of solution *A* to 2 grams of the finely-powdered nitre, shake, and place the tube in front of a sheet of white paper. If 0·1% of chlorate is present, an intense blue coloration is produced immediately. With 0·01%, the coloration appears before five minutes, and with 0·009 to 0·005%, before ten minutes. If a coloration is not produced within thirty minutes, the proportion of chlorate is less than 0·001%. The urine test (Abstr., 1909, ii, 432) can also be applied to detect chlorates in refined nitres.

Quantitative.—Twenty grams of the nitre are made up to 100 c.c. with water, the solution being filtered if necessary through a dry filter, and 10 c.c. added to a graduated cylinder. In a second cylinder, 2 c.c. of a solution containing 0·1 gram of potassium chlorate per litre are mixed with a saturated solution of pure nitre free from chlorate so as to make 10 c.c. To each solution, 15 c.c. of reagent *B* are then added, the solutions are thoroughly mixed, and examined colorimetrically after twenty-five to thirty minutes. The solutions are diluted until the shades are equalised. If the nitre contains more than 0·02% of chlorate, 4 c.c. or more of the standard chlorate solution are taken.

With sodium nitrate the procedure is similar to that described for nitres, but a stronger solution can be used in the case of samples containing less than 0·01% of chlorate, owing to sodium nitrate being more soluble than potassium nitrate.

Explosives.—Explosives intentionally chlorated show the presence of chlorate when 0·01 gram is dissolved in 8—10 drops of water and 2 c.c. of solution *B* added. Generally, explosives contain chlorate only as an impurity. In such cases, 4—5 grams are digested with water, the solution filtered, and evaporated to dryness; the residue is powdered and examined as a refined nitre.

Quantitative.—One gram of the explosive is dissolved in sufficient water (filtering if necessary) to give a solution containing approximately 0·5 gram of chlorate per litre. Five c.c. of the solution are mixed with 20 c.c. of the solution *B* in a graduated cylinder of 50 c.c., and the colour compared with 5 c.c. of a solution of 0·5 gram of pure potassium chlorate in 1 litre, similarly treated with 20 c.c. of *B*. The solutions are diluted with a mixture of 4 vols. of *B* with 1 vol. of water until the shades are equalised. Having approximately obtained the percentage of chlorate in this way, the exact proportion can then be ascertained by preparing a suitable scale of comparison shades in 100 c.c. cylinders. W. A. D.

The Estimation of Alkalis in Silicates by the Lawrence Smith Method. THEODOR DÖRING (*Zeitsch. anal. Chem.*, 1910, **49**, 158—172).—A series of analyses of silicates by the process recommended by Lawrence Smith (ignition with ammonium chloride and calcium carbonate and boiling the mass repeatedly with water).

The author finds that the last portions of the alkali chlorides are somewhat obstinately retained by the insoluble mass, and that when 0·5—0·6 gram of the silicate has been taken, the volume of the filtrate should not be less than 400—500 c.c.

The method is recommended also for those silicates which are readily decomposed by hydrochloric acid, as the process involves no separation of silica, aluminium, iron, and magnesium. For highly basic slags, the process seems, however, less suited.

L. DE K.

Apparatus for Testing Gypsum. JACOBUS H. VAN'T HOFF (*Zeitsch. physikal. Chem.*, 1910, **70**, 146—152).—A form of dilatometer

by means of which specimens of gypsum may be tested as regards the rate with which they absorb water is described and figured. It consists of a conical vessel, to one side of which is attached, by means of a short piece of glass tube, a long, graduated capillary tube. The glass tube contains a piece of cotton wool, which serves as a filter to prevent gypsum entering along with water into the capillary tube. In making an experiment, a definite weight of water saturated with gypsum is added to a definite quantity of gypsum, the vessel tightly corked, and the rate at which the gypsum combines with water deduced from the motion of the latter in the graduated capillary.

The first experiment was made with a specimen of the half-hydrate, $2CaSO_4,H_2O$. When a small correction was applied for the initial disturbance due to the dissolving of the half-hydrate in water saturated with gypsum, it was found that the maximum velocity of combination was attained in about sixty-eight minutes at 19°, and that this corresponded with the stage at which the reaction was half completed. This may be anticipated if the rate of combination is proportional both to unaltered half-hydrate, $1-x$, and to the amount transformed, x. An experiment with a specimen of natural gypsum showed that in this case, also, the maximum rate of contraction coincides with half-transition, although there are considerable initial disturbances, due probably to capillaries in the gypsum which become filled with water at the beginning of the experiment. For a specimen of gypsum supplied as "Estrich gypsum," which combined with water very slowly, the rate of combination after the first day was represented by the equation: $-dx/dt=k(1-x)$, being simply proportional to the proportion of gypsum present.

The relationship between the quality of gypsum and its rate of combination with water has not been investigated. G. S.

Volumetric Estimation of Zinc and Cyanogen. HERMANN GROSSMANN and LOTHAR HÖLTER (*Chem. Zeit.*, 1910, **34**, 181—182).—To a solution containing about 0·5 gram of the zinc salt are added 2—5 c.c. of ammonium chloride (250 grams per litre) and also 1 c.c. of 20% potassium iodide and 0·5—1 c.c. of silver nitrate (5·85 grams per litre), and the liquid is then at once titrated with standardised potassium cyanide until the turbidity due to silver iodide disappears. The titration process fails in ammoniacal solution, but with neutral solutions the results are accurate. A joint estimation of zinc and nickel may be made in this manner. As nickel may be estimated accurately with potassium cyanide, the authors tried to estimate potassium cyanide conversely with nickel solution. Fairly accurate results are obtained by simply adding the nickel solution of known strength to the cyanide until a permanent precipitate of nickel cyanide is formed. L. DE K.

Test for Cadmium in the Presence of Copper by means of Hydrogen Sulphide. LOTHAR WÖHLER and Z. VON HIRSCHBERG (*Ber.*, 1910, **43**, 753—754).—In the course of ordinary qualitative analysis, when hydrogen sulphide is passed into the ammoniacal cyanide solution which may contain cadmium as well as copper, an

orange-red precipitate is often formed in small quantity, even when cadmium is absent. The precipitate closely resembles that of antimony sulphide, but it is soluble in alcohol, and has the composition $C_2H_4N_2S_2$. It is identical with dithio-oxamide (compare Formánek, Abstr., 1890, i, 29). The formation of this precipitate is favoured by a low temperature, but hindered by using an excess of potassium cyanide beyond that necessary to decolorise the ammoniacal copper solution.

T. S. P.

Micro-chemical Estimation of Mercury. P. E. RAASCHOU (*Zeitsch. anal. Chem.*, 1910, **49**, 172—204).—The process is briefly as follows: the liquid treated previously, if necessary, with hydrochloric acid and potassium chlorate is precipitated with hydrogen sulphide; addition of a little copper sulphate is advantageous. The precipitate is collected on a small asbestos filter, and then burnt in a special apparatus with lead chromate, the last traces of mercury being swept out by a current of carbon dioxide generated from magnesite or manganous carbonate; lead peroxide, which yields oxygen, may also be used.

The mercury which condenses in the capillary tube may be united to one or more little globules by treatment with hot hydrochloric acid; D 1·17. After drying with filter paper, the globule (or globules) of mercury is carefully examined under the microscope, and the horizontal diameter is measured with a micrometer. Reference is then had to a table to find the corresponding weight.

L. DE K.

Volumetric Separation of Mercury and Silver. ERWIN RUPP and F. LEHMANN (*Chem. Zeit.*, 1910, **34**, 229—230).—*Estimation of Mercury only in Presence of Silver.*—A suitable quantity of the nitric acid solution is mixed with an alkaline solution of potassium iodide, made up to a definite volume, and filtered. To 50 c.c. of the clear filtrate is added 15 c.c. of dilute sodium hydroxide, 3 c.c. of strong formaldehyde, and 10 c.c. of water. After shaking for five minutes, 10 c.c. of glacial acetic acid are added, and also 25 or 50 c.c. of *N*/10-iodine. When all metallic mercury has disappeared, the excess of iodine is titrated as usual with *N*/10-thiosulphate.

Joint Estimation of Mercury and Silver.—The same quantity of the solution is mixed with 2—3 c.c. of iron-alum, and so much colourless nitric acid is added that the iron colour becomes invisible. The solution is then titrated with *N*/10-thiocyanate as usual.

L. DE K.

New Reaction for Thallium. SEBASTIAN TANATAR and S. PETROFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 94—95).—Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, serves as a very sensitive reagent for thallium in slightly acid solution, giving a red, crystalline precipitate of thallium cobaltinitrite, $Th_3Co(NO_2)_6$, which is insoluble in hot water or in cold dilute acids. On boiling with acids, the precipitate dissolves with evolution of oxides of nitrogen, thallium and cobalt salts passing into solution. Thallium cobaltinitrite is slightly more soluble than the iodide, one part dissolving in 10,000 parts of water. The only other metal which forms a precipitate with sodium cobaltinitrite is lead, the precipitate in this case being unstable and readily soluble in water.

The formation of thallium cobaltinitrite may also be used for the detection of cobalt and for its separation from nickel. The precipitate is formed even in dilute solutions of a cobalt salt (0·02*N*) by addition of excess of sodium nitrite, acetic acid, and thallium nitrate; nickel is not precipitated under these conditions. T. H. P.

Estimation of Manganese by the Volhard-Wolff Process. EUGEN DEISS (*Chem. Zeit.*, 1910, **34**, 237—238).—A slight modification of the above process. *First Process.*—For ten parts of ferric chloride not more than one part of manganous chloride should be present. The solution, concentrated if necessary, is carefully neutralised with potassium carbonate, and diluted with boiling water to 600 c.c.; a small excess of standard permanganate is added, and the whole well shaken. An emulsion of zinc oxide is added to precipitate both iron and manganic oxides. The excess of permanganate is then estimated by a suitable method.

Second process.—The solution is diluted with boiling water to 600 c.c., and precipitated with zinc oxide emulsion. A previously-measured excess of permanganate is then added all at once without delay, and when the precipitate has settled, the free permanganate is titrated as before. L. DE K.

Titrimetric Estimation of Ferrous Oxide and Boric Acid in Silicates. JOHANNES FROMME (*Tsch. Min. Mitt.*, 1909, **28**, 329—333). —For the determination of ferrous iron, the powdered silicate is decomposed by sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, as in the usual method; but instead of expelling the excess of hydrofluoric acid by evaporation, it is quicker to neutralise by the addition of pure silica. The resulting hydrogen silico-fluoride has only a slow action on the potassium permanganate used in the titration.

Boric acid may be estimated conveniently in boro-silicates, such as axinite and datolite, by fusing the mineral with alkali carbonates and titrating with sodium hydroxide in the presence of suitable indicators. The hot aqueous solution of the carbonate-melt is saturated with carbon dioxide, silica filtered off, and the filtrate reduced to a small volume; hydrochloric acid is added, and then 96% alcohol to expel the carbon dioxide without heating; the silica is again filtered off, and the hydrochloric acid neutralised with *N*/2-sodium hydroxide, using dimethylaminoazobenzene as an indicator. Neutral glycerol is now added, and the free boric acid titrated with *N*/10-sodium hydroxide until the indicator (dimethylaminoazobenzene + phenolphthalein) shows a rose-red. L. J. S.

Estimation of Iron in Ferric Solution. ALFRED F. JOSEPH (*J. Soc. Chem. Ind.*, 1910, **29**, 187).—Fairly accurate results may be obtained by simply acidifying the ferric solution with hydrochloric acid, adding a few grams of potassium iodide, and titrating the iodine liberated at once with standard thiosulphate. Unless a coloured compound is present, the author does not use starch as indicator, but simply depends on the disappearance of the iodine colour.

L. DE K.

Analysis of Cobalt and Nickel. FRANZ FELIX WERNER (*Pharm. Zeit.*, 1910, **55**, 211—212).—The black sulphides of nickel or cobalt obtained in the ordinary course of analysis are dissolved in a little nitrohydrochloric acid, the solution is evaporated to dryness, and the residue taken up with water and a little hydrochloric acid. To a little of the solution is then added ferrocyanide solution. With cobalt, a dark green precipitate is obtained, and in extremely dilute solutions a decided green coloration is noticed. The compound is, however, very unstable, and is rapidly oxidised.

Nickel solutions are precipitated quantitatively. The precipitate has an apple-green colour, and is very stable. L. DE K.

Gravimetric Methods for the Estimation of Nickel in Nickel Steel. EZRA L. RHEAD (*Analyst*, 1910, **35**, 97—103).—The acetate separation of iron from nickel gives good results if care is taken to fully neutralise the solution before boiling with sodium acetate, without, however, causing a permanent precipitate. If the presence of ammonium salts does not interfere with the subsequent precipitation of the nickel, ammonia may be used, otherwise sodium hydroxide must be used. The ammonia process of separation is untrustworthy even in the presence of potassium cyanide; in the latter case, the precipitation may be effected by substituting sodium hydroxide for ammonia. The filtrate contains all the nickel, which may then be precipitated as the higher oxide by means of sodium hypobromite; or the filtrate may be evaporated with sulphuric acid, and the nickel deposited electrolytically in ammoniacal solution. The bulk of the iron may, if desired, be removed from the solution of the chlorides in hydrochloric acid, D 1·125, by shaking with ether, and the remaining iron precipitated with alkaline cyanide. The most rapid process, however, is the precipitation of nickel in ammoniacal solution with a large excess of an alcoholic solution of dimethylglyoxime (Iwanicki's process). L. DE K.

Estimation of the Acid Radicle in Commercial Bismuth Subnitrate. JOHN B. P. HARRISON (*Analyst*, 1910, **35**, 118—124).—An investigation as to the composition of commercial bismuth subnitrate, which is supposed to be somewhat variable. The author, however, was not successful in demonstrating any sensible differences in the composition of various samples. The simplest formula is $6Bi_2O_3,5N_2O_5,8\frac{1}{2}H_2O$.

Brown's indirect method for estimating the nitric radicle, conversion into oxychloride (Abstr., 1908, ii, 391) is recommended. The "nitron" method is also useful, and as a check the nitrometer may be employed. L. DE K.

[Estimation of] Antimony Hydride. HANS RECKLEBEN and A. GÜTTICH (*Zeitsch. anal. Chem.*, 1910, **49**, 73—82).—The results obtained by the authors may be summarised as follows: Contrary to general belief there is really no difference between the action of antimony and arsenic hydrides on silver nitrate, metallic silver being deposited in either case. Owing, however, to the sparing solubility of

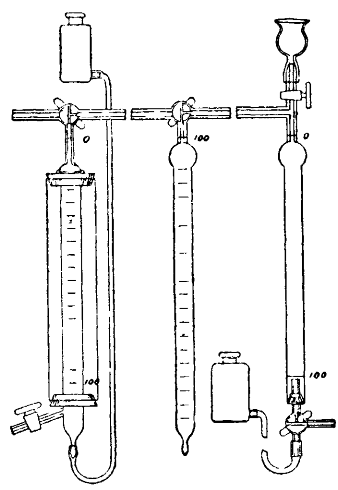
antimony oxide, a portion of this contaminates the silver, which, therefore, cannot be weighed and calculated into antimony.

Antimony hydride is readily attacked by fixed and earthy hydroxides with formation of metallic antimony, whereas arsenic hydride is but partially resolved into metallic arsenic. The best absorbents for antimony hydride, when not too much diluted, are silver, iodine and iodic acid solutions, also a strong solution of mercuric chloride. The antimony may then be recovered from the absorbent by a suitable process, or, if iodine has been used, it may be found indirectly by titrating the iodine before and after the absorption; or the antimony hydride may be found simply by noting the decrease in volume of the antimonial gas mixture after absorption. L. DE K.

Estimation of Osmium. OTTO RUFF and FERD. BORNEMANN (*Zeitsch. anorg. Chem.*, 1910, **65**, 429—456).—See this vol., ii, 305.

Elementary Analysis of Difficultly Combustible Substances Rich in Carbon. KARL HOLDERMANN and ROLAND SCHOLL (*Ber.*, 1910, **43**, 342—343).—See this vol., i, 285.

Analysis of Illuminating Gas. A. H. ELLIOTT (*J. Soc. Chem. Ind.*, 1910, **29**, 192—193).—The gas is collected by opening the stopcocks of a 200 c.c. tube filled with water, thus allowing the gas to flow in. By reversing the operation, the gas is forced into the apparatus (see Fig.). The first tube into which it is drawn has a mark below, indicating that 100 c.c. of gas are taken in excess of the amount required. Gas is then introduced by the aspirator bottles into the middle graduated tube, and measured accurately, arranging the bottles so that the water in the lower one is level with that in the tube; and after the upper stopcock is closed, the excess of gas in the first tube is rejected through the funnel. The water must be used at a constant temperature. The reagents are introduced by means of the funnel which fits on the outside of the end of the stopcock on the first tube, called the laboratory tube. When transferring 100 c.c. from the middle tube to the laboratory tube, the water is driven over from the middle tube, until it occupies a position marked on the capillary part of the laboratory tube above. Owing to the peculiar shape of the bulb, the gas is pulled down at the sides by the reagents used, and returns up to the middle of the tubes, causing a circulation. A few drops of the reagent make an enormous surface, and cause a rapid absorption of the gas. The reagents employed are 20% sodium hydroxide to absorb carbon



dioxide, bromine to absorb benzene and other illuminants, then, after removing the excess of bromine, alkaline 10% pyrogallol to absorb oxygen, whilst carbon monoxide is removed by means of a hydrochloric acid solution of cuprous chloride. The gas after each absorption is not measured at once, but the tube is allowed to drain; the lower and upper stopcocks on the laboratory tube are opened, the reagent is allowed to drain out, and the tube is washed with clean water.

The residual gas (hydrogen, nitrogen, and methane) is usually exploded with excess of oxygen, but the author found that nitrogen is also oxidised. Twelve to thirteen c.c. are transferred to the jacketed explosion tube, and then mixed with six to seven times the volume of air; in this way there is no danger of nitrogen being affected. If on final treatment with alkaline pyrogallol there is no absorption, the operation must be repeated, using a larger volume of air.

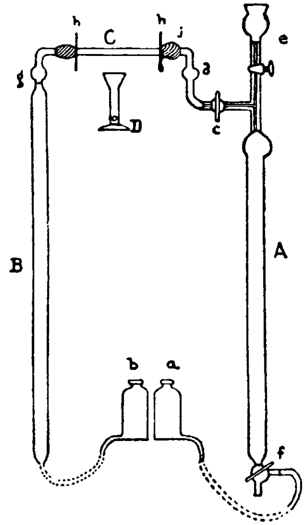
The hydrogen and methane are found as usual from the contractions after explosion, and subsequent treatment with sodium hydroxide. From the volume of the residual nitrogen is deducted the nitrogen due to the air introduced. L. DE K.

The Elliott Gas Analysis Apparatus. E. C. UHLIG (*J. Soc. Chem. Ind.*, 1910, **29**, 194—195).—The apparatus and process used by Elliott (see preceding abstract) are recommended for rapid work. In an experiment made by the author, using both Elliott's and Hempel's process, the results agreed fairly well, except as regards methane and nitrogen: Elliott (19·6% methane, 6·3% nitrogen); Hempel (17·5% methane, 9·1% nitrogen). L. DE K.

Oil-Gas Analysis Apparatus. E. C. UHLIG (*J. Soc. Chem. Ind.*, 1910, **29**, 196—197).—The apparatus consists of an absorption tube, *A*, connected with the piece *cd*. This is made of tubing 1 mm. internal diameter to the bottom of the upright part, *d*, which has an internal diameter of 6 mm. and an external one of 10 mm.; the bulb is 15 mm. external diameter. The tube *A* may be graduated. The tube *B* has a capacity of 100 c.c., and is graduated to 0·1 c.c. It is contracted below the bulb *g*, which is 15 mm. external diameter. *C* is a quartz tube filled with fine granular copper oxide; its ends are plugged with asbestos fibre. The connexion with *A* and *B* is made with india-rubber tube wired on and covered with wet lamp wick, as shown at *jj*; this must be kept wet during the combustion. Two disks of asbestos board, through which passes the tube *C*, are indicated by *h h*. *C* is heated by the burner *D*.

When required, *A* and *B* are filled with water by raising the bottles *a* and *b*, which are attached to the tubes by india-rubber tubing. The apparatus is then filled with nitrogen from the cock *c* to the narrow part under *g*. This is done by lowering the bottle *a* and opening the cock *e*, thus admitting air into *A*; *e* is then closed, and the funnel filled with alkaline pyrogallol, which is gradually lowered into *A*. When all the oxygen has been absorbed in *A*, *c* is

opened, and the nitrogen passed from A to B and back several times, applying alkaline pyrogallol when the nitrogen is in A. b is raised, so that the level of the water is at the narrow part of B under g. When the water at B is at this mark, c is closed, the three-way cock f opened to drain A, and e is also opened. A is then emptied and washed out, and a filled with fresh water. It is then raised above e, and when A is filled, c is closed. The funnel is removed, and exactly 100 c.c. of gas are introduced into A, and subjected to the usual absorption tests. When, finally, only hydrogen, methane, and nitrogen are left, the gas is transferred to B, and the cock c is closed. A and a are now refilled with water. D is lighted, and a small flame permitted to burn three inches below C. The gas is passed from B to A and back six or eight times. The burner is removed and the quartz tube cooled with water, and a reading is then taken by raising b until its water level coincides with that in B. The contraction equals the hydrogen, methane not being affected by copper oxide below 250°. C is now raised to a red heat, the funnel is filled with 10% sodium hydroxide solution, and the gas passed from B to A and back; when in A, c is closed, and sodium hydroxide admitted. When no more contraction is observed, the burner is removed, and when cold, the nitrogen in B is measured. The methane is found by difference, and may include any ethane if present.

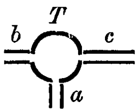


L. de K.

An Improvement in Fresenius' Method for Estimating Hydrocarbons in Gases. Ferdinand Henrich (*Zeitsch. angew. Chem.*, 1910, **23**, 441—446).—In 1886, R. Fresenius found 0·053 volume % of light hydrocarbons in the gases from the Wiesbaden Hot Spring, and in 1906 Grünhut and Hintz found 0·28 vol. % of methane. More recent determinations by the author give 0·53 vol. % of methane. The method adopted for estimating the methane was a modification of that introduced by Fresenius, namely, passing a given volume of the gas over heated oxide of copper and weighing the carbon dioxide formed.

A layer of oxide 75 cm. long is recommended in place of Fresenius's 25 cm. A given volume of the gas, free from carbon dioxide and oxygen, is placed in a Bunte burette, which is attached to the arm, b, of the bulb-T-tube, T; the side-tube a is attached to a wash-bottle containing concentrated potassium hydroxide solution, and then to a gas-holder containing air, and the tube c to two wash-bottles, one containing potassium hydroxide solution, and the other concentrated sulphuric acid and then to a long double U-tube containing soda-lime

and granular calcium chloride; this is followed by the combustion tube containing the oxide of copper, and then come the usual calcium chloride tube and potash bulbs, which are attached to a calcium chloride tube and aspirator. The gas is passed from the Bunte burette through the apparatus, so that 100 c.c. require some fifteen to twenty minutes; two litres of air are then aspirated through the apparatus, which is then disconnected, and the calcium chloride tube and potash bulbs weighed.



The bulb-T serves to catch drops of water which pass over from the burette.

The following results were obtained with the gases from the springs mentioned: Hot Spring, 0·53; Schützenhof Spring, 0·77, 0·41; Adler Spring, 0·77; Golden Spring, 0·45% methane at 0° and 760 mm.

In the analyses it is not necessary to use 900—1000 c.c. of gas, as recommended by Grünhut and Hintz; 100 c.c. is quite sufficient.

A form of apparatus for collecting gases is described, and also an apparatus for freeing large volumes of gas from carbon dioxide.

J. J. S.

Improved Method for Analysis of Gases from Mineral Springs. ERNST HINTZ and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1910, **49**, 25—42).—A lengthy paper, giving detailed results of analyses of gases from mineral springs, and also dealing with radioactivity of mineral waters. The chief point of interest is the estimation of methane, which is effected in the usual way by combustion of a large quantity of the gases freed previously from carbon dioxide. A combustion tube, 75 c.c. long, filled with copper oxide and connected with the usual train of calcium chloride and soda-lime tubes, is recommended.

The gases are best collected in a Weinhold suction flask containing 12% aqueous potassium hydroxide.

L. DE K.

Reduced Alcoholometry. ANTOINE DE SAPORTA (*Bull. Soc. chim.*, 1910, [iv], **7**, 70—71).—If the usual quantity of distillate is collected in estimating the alcohol in weak wines, either a weak distillate is obtained or a larger quantity of wine than usual must be used, necessitating the expenditure of a longer time in carrying out the estimation. To avoid this difficulty, the author distils only 60 c.c. into the ordinary test glass and then places in this, discs of ebonite each having a hole in the centre large enough to allow the stem of the hydrometer to pass through. In this way hydrometer readings can be obtained with the smaller volume of distillate.

T. A. H.

Analysis of Turpentine Oils. PAUL NICOLARDOT and LOUIS CLÉMENT (*Bull. Soc. chim.*, 1910, [iv], **7**, 105—109).—For the detection of badly prepared, old, or adulterated turpentine oils, the author recommends the determination of (1) the acid number, (2) residue left on distillation up to 59° under 180 mm. pressure, (3) refractive index, (4) flash point, and (5) optical rotation of each of five equal fractions,

collected from 50° to 59° under 180 mm. pressure. Particulars of the results obtained with several turpentine oils are given in the original.
T. A. H.

New Method of Analysis by Miscibility Curves; Application to Turpentine Oils. ÉMILE LOUÏSE (*Compt. rend.*, 1910, **150**, 526—528. Compare Abstr., 1907, ii, 722; 1909, ii, 722).—The method already described can be applied to the analysis of commercial turpentine, when it readily reveals the presence of adulterants, such as light petroleum and resin oils. Instead of the acetone employed in previous experiments, aniline is used to mix with the liquid under examination. The miscibility curves are given for mixtures of aniline with French turpentine and with the above-mentioned adulterants. The method has also been applied to the analysis of petroleum oils, alcohols, perfumes and pharmaceutical preparations, and also to the determination of molecular weight.
W. O. W.

The Estimation of Invert Sugar in Sugar Beets. JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 287—297).—The ordinary Fehling's solution does not give absolutely accurate results with sugar-beet extracts, and a modification is therefore proposed; 34·64 grams of copper sulphate are dissolved in 500 c.c. of water to form one solution. The other is composed of 173 grams of sodium potassium tartrate and 178 grams of crystalline sodium carbonate (or 66·1 grams of the anhydrous salt) in 500 c.c. of water. A table is given showing the relation between the copper precipitated and the invert sugar present. Certain details of manipulation are also discussed.
E. J. R.

Detection of Traces of Formaldehyde in Presence of Acetaldehyde by Schiff's Reagent. GEORGES DENIGÈS (*Compt. rend.*, 1910, **150**, 529—531).—Differences in the behaviour of Schiff's reagent towards acetaldehyde and formaldehyde enable the latter to be detected when present to the extent of one part in 10,000 of acetaldehyde; 5 c.c. of an aqueous solutions containing not more than 2% acetaldehyde are mixed with 1·2 c.c. of pure sulphuric acid (D 1·66) and 5 c.c. of Schiff's reagent. Under these conditions, if the aldehyde is pure, no coloration is observed, but if formaldehyde is treated in the same way, the liquid becomes intensely violet and shows an absorption band in the orange. The Schiff's reagent is best prepared by adding a litre of a 0·01% solution of magenta to 20 c.c. of sodium hydrogen sulphite solution (D 36—40° Baumé), and, after five minutes, adding 20 c.c. of hydrochloric acid (D 1·18).

The method is recommended for determining the presence of formaldehyde or its derivatives in wine, and for the estimation of methyl alcohol in denaturated spirits.
W. O. W.

[Modification of Rimini's Test for Formaldehyde.] SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1910, *B*, **82**, 226—232).—See this vol., ii, 334.

Janovsky's Reaction for Dinitro-compounds, and Bitto's Reaction for Aldehydes and Ketones with Aromatic Compounds. FRITZ REITZENSTEIN and GEORG STAMM (*J. pr. Chem.*, 1910, [ii], **81**, 167—176).—When a solution of 1-chloro-2 : 4-dinitrobenzene in acetone is slowly added to sodioacetone in a current of hydrogen, a deep violet coloration is produced, and, finally, a brown precipitate. The latter, after purification, consists of a brown *powder*, $C_9H_8O_5N_2$, m. p. 95—105°, which is probably $CH_2{:}CMe{\cdot}O{\cdot}C_6H_3(NO_2)_2$. The substance accounts for the intense bluish-violet colour produced by the addition of potassium or sodium hydroxide to an acetone solution of 1-chloro-2 : 4-dinitrobenzene. The reaction is an instance of Janovsky's test for dinitro-compounds (Abstr., 1891, 685), which was extended by Bitto (Abstr., 1892, 1263) to apply as a test for aldehydes and ketones. Bitto's reaction is almost unmentioned in the literature. The authors now tabulate the colour reactions given by numerous nitro-compounds with acetone and potassium hydroxide, and also those exhibited by *m*-dinitrobenzene, potassium hydroxide, and aliphatic and cyclic substances containing the group $\cdot CH_2 \cdot CO$. C. S.

Direct Test for Acetone in Urine. BRUNO BARDACH (*Zeitsch. anal. Chem.*, 1910, **49**, 103—106).—The author has applied his iodine test for acetone (Abstr., 1909, ii, 626) to the detection of acetone in urines without previous distillation. To 3 c.c. of filtered urine is added 1 c.c. of a 3% solution of pure peptone, then Lugol's solution (4 grams of iodine, 6 grams of potassium iodide, 100 c.c. of water) until the liquid is dark brown, and finally 2 c.c. of ammonia. If a sufficiency of iodine is present, the colour should persist for about ten minutes; if not, some more iodine should be added, or, better still, a new mixture should be made. After an hour and a half, the liquid is acidified with hydrochloric acid, and if the solution gets quite clear, acetone is absent. Any excess of iodine may be bleached with a few drops of dilute thiosulphate. Any precipitate must then be examined under the microscope, when it should have the appearance of delicate needles, either individually or in clusters. L. DE K.

A Possible Significance of the Cammidge Reaction. LEYMAN B. STOOKEY (*Proc. Amer. physiol. Soc.*, 1909, 14—15; *Amer. J. Physiol.*, **25**).—Smolenski attributes the Cammidge reaction to sucrose in the urine (Abstr., 1909, ii, 598), and the experiments given show that there may be some relationship between the amount of sucrose in the food and the intensity of the reaction. W. D. H.

The Pancreas Reaction of Cammidge. HANS ELLENBECK *Biochem. Zeitsch.*, 1910, **24**, 22—39).—The author gives details of the various methods he employed in carrying out this reaction, and also of the appearances, melting points, and solubilities of the crystals obtained in various cases. In applying the reaction to twenty-four cases of healthy children, and children suffering from alimentary disturbances, it was found that the reaction was almost always positive in the case of the ailing children. In normal cases, however, the reaction is sometimes positive. The conclusion is drawn that the

positive reaction cannot be accepted as indicative of diseases of the pancreas. S. B. S.

Uffelmann's Lactic Acid Reaction. HUGO KÜHL (*Milchw. Zentr.*, 1910, **6**, 61—63; *Pharm. Zeit.*, 1910, **55**, 120—121).—Uffelmann's test for lactic acid is as follows: 10 c.c. of a 2% solution of phenol are mixed with a few drops of ferric chloride. The amethyst-blue solution turns lemon-yellow if a liquid containing lactic acid is added The author, however, noticed that this reaction is not characteristic for lactic acid, and that tartaric, citric, malic, and oxalic acids also give it. Lævulic and benzoic acids do not give the reaction.

If, however, used for the identification of a group of acids, Uffelmann's test may be improved by substituting a 1/400% solution of salicylic acid for phenol. Benzoic acid may also be employed as follows: 5 c.c. of its solution (1:500) are mixed with a drop of ferric chloride (1 : 10), when a white turbidity with a green reflexion is formed. On adding a few drops of a weak solution (1 : 1000) of lactic, tartaric, citric, malic, or lævulic acid, the liquid becomes clear and turns a dark greenish-yellow. Curiously the reaction is also given by ammonium oxalate. In this case the green predominates. L. DE K.

New Method for Estimating *d*-Tartaric Acid. ANDRÉ KLING (*Compt. rend.*, 1910, **150**, 616—618).—The following method is recommended for estimating *d*-tartaric acid in wines or natural products.

Twenty-five c.c. of the solution containing 3 to 4 grams per litre of *d*-tartaric acid are treated with 100 c.c. of water and 25 c.c. of a 1·6% solution of pure Rochelle salt and 20 c.c. of a 5% solution of calcium acetate. The precipitated calcium racemate contains a small quantity of optically active salt, and is dissolved in 20 c.c. of 4% hydrochloric acid, diluted to 150 c.c., and the solution heated to boiling with 40 c.c. of a solution containing sodium acetate (10%) and calcium acetate (1%). After cooling the precipitate is filtered off, dissolved in boiling hydrochloric acid (10%), and titrated with a 1·6% solution of potassium permanganate.

The results are somewhat higher than those obtained by the usual method. Phosphates, sulphates, sulphites, calcium salts, acetic, malic and succinic acids, dextrose, tannin, and colouring matters do not interfere with the method. Salts of iron or aluminium prevent precipitation of the calcium racemate. Tartaric esters give no precipitate under these conditions. W. O. W.

Detection of Benzoic, Cinnamic, and Salicylic Acids in Wine. KARL VON DER HEIDE and F. JAKOB (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 137—153).—The following processes may be used for identifying these three acids when present together in wine: a portion of the latter is first extracted with chloroform in the usual way, and the presence of salicylic acid detected by means of ferric chloride. A second portion of the wine is then rendered alkaline, evaporated, acidified, and extracted with ether. The ethereal extract is shaken

with alkali solution in order to obtain the organic acids present in aqueous solution. This solution is heated until all dissolved ether has been removed, and, when cold, is treated with a few drops of 1% potassium permanganate solution. The mixture is heated on a water-bath, and should as little as 0·01 mg. of cinnamic acid be present, an odour of benzaldehyde will be noticed. The addition of permanganate is then continued until the oxidation is complete, the benzaldehyde being converted into benzoic acid, and the salicylic acid, if present, completely destroyed. After removing the excess of permanganate by the addition of sulphurous acid, the acidified solution is extracted with ether, and the residue obtained on evaporating the ethereal extract is tested for benzoic acid (resulting from the oxidation of the cinnamic acid in addition to any benzoic acid actually present as such) as described by Robin (Abstr., 1908, ii, 1078). The presence of benzoic acid itself may be ascertained by submitting the acidified wine to steam distillation and applying Robin's test to the ether extract of the distillate. The authors have also made experiments regarding the comparative antiseptic effect of benzoic, cinnamic, and salicylic acids; they find that the following quantities of the respective acids are required to inhibit fermentation in wine must containing yeast: benzoic acid, 0·15 to 0·25 gram; salicylic acid, 0·10 to 0·25 gram; and cinnamic acid, 0·05 to 0·15 gram per litre. W. P. S.

Fat Extraction Apparatus. A. van Raalte (*Chem. Weekblad*, 1910, 7, 191).—A description of an apparatus for extracting fat from flour with carbon tetrachloride. A. J. W.

New Method of Estimating Margarine in Butter. M. Raffo and G. Foresti (*Gazzetta*, 1909, 39, ii, 441—444).—The authors find that the presence of margarine in butter may be detected by measuring its viscosity. Using an Ostwald viscosimeter at 50°, the time of efflux for water was 32·6 seconds, whilst for each of five samples of butter it was 66·4 secs., and for margarine, 85·8 secs. A number of mixtures of butter and margarine were examined; the presence of 10% of margarine raises the time of efflux from 66·4 to 68·4 secs. T. H. P.

Chemical and Viscosimetric Investigations on Animal Fats. M. Raffo and G. Foresti (*Gazzetta*, 1909, 39, ii, 444—449).—Fats from different animals exhibit different constants, but with fats from different parts of the same animal this does not appear to be the case. The curves connecting the viscosity constant η with temperature for six different animal fats follow approximately parallel courses from 60° to 80°. T. H. P.

Estimation of the Acid and Saponification Numbers in Dark-coloured Oils and Fats. F. Marx (*Chem. Zeit.*, 1910, 34, 124).—2·5 Grams of the sample are placed in a 600 c.c. porcelain dish and well stirred with addition of 50 c.c. of neutral alcohol, and, after adding 6—8 drops of phenolphthalein solution, the free acidity is titrated. The whole is then transferred to a 250 c.c. flask, and the dish is rinsed first with 20 c.c. and then again twice with 10 c.c. of

benzene. Twenty-five c.c of $N/2$-alcoholic potassium hydroxide are added, and the mixture is boiled, as usual, for half an hour. The contents are now returned to the dish, the flask is well washed with hot alcohol until the total volume is about 150 c.c., and, after adding another 4—6 drops of phenolphthalein, the excess of alkali is titrated. The end reaction is very sharp, even with fish oils. During the titration the liquid should be well stirred with a glass rod.

L. DE K.

Estimation of Acid and Saponification Numbers in Dark-coloured Oils and Fats. FRIEDRICH MAYER (*Chem. Zeit.*, 1910, **34**, 238—239).—The process, which aims at the determination of tallow in cylinder oil, is carried out as follows: 10 grams of the oil are dissolved in a 200 c.c. flask in 25 c.c. of benzene, and gently boiled for an hour with 25 c.c. of (? alcoholic) $N/2$-potassium hydroxide; 30 c.c. of water are then added, and the whole introduced into a separating funnel; the alkaline liquid is drawn off, and the benzene layer washed twice in succession with 25 c.c. of water. The excess of alkali is then titrated as usual, using phenolphthalein as indicator. Although the liquid is slightly yellow and milky, the end reaction is very distinct.

L. DE K.

Analysis of Ferrocyanides. FREDERICK W. SKIRROW (*J. Soc. Chem. Ind.*, 1910, **29**, 319—323).—A review of Colman's paper (*Analyst*, 1908, **33**, 261) on the various processes of estimating ferrocyanogen in spent iron oxides, etc. The following conclusions are arrived at:

In the Feld method, a loss of hydrogen cyanide occurs on boiling the alkaline ferrocyanide with excess of magnesium chloride. A practical recovery of hydrogen cyanide takes place on distilling mercuric cyanide with dilute sulphuric acid in presence of chloride, but owing to impurities usually present, there is generally some loss. When using the zinc sulphate process, it is better to have the solutions a little more concentrated than usual. In the separation of ferrocyanide from carbonyl ferrocyanide, it is advisable to wash the precipitate with absolute alcohol, and to titrate directly in the presence of the filter.

When working with spent iron oxide previously extracted with carbon disulphide, the alkaline solution should be well boiled to separate the iron properly, and then be filtered. Traces of ferrocyanide, however, always remain in the insoluble residue, probably in the form of the calcium-iron compound. L. DE K.

Estimation of Betaine. VLADIMIR STANĚK and K. DOMIN (*Zeitsch. Zuckerind. Böhm*, 1910, **34**, 297—304).—See this vol., ii, 336.

Application of the Volhard Method to the Estimation of Alkaloids. ELIAS ELVOVE (*J. Amer. Chem. Soc.*, 1910, **32**, 132—139). —The estimation of alkaloids can be much simplified by converting them into their hydrochlorides and estimating the chlorine by the Volhard method. In an earlier paper (*Bull.* 54, *Hyg. Lab., U.S. Pub. Health and Mar. Hosp. Serv.*), the author has applied this method to

quinine, quinidine, cinchonine, cinchonidine, and strychnine. In the present work its use has been extended to cocaine, morphine, codeine, narcotine, atropine, hydrastine, pilocarpine, and brucine.

The amount of alkaloid in specimens obtained commercially or in the course of assay may be estimated in the following way. About 0·2 gram is dissolved in 20 c.c. of 4% hydrochloric acid, the liquid is evaporated to dryness on the water-bath, and the residue is mixed with 5 c.c. of alcohol and again evaporated, this treatment with alcohol being repeated. The residue is dissolved in about 10 c.c. of water, and the solution titrated with standard alkali in presence of phenolphthalein. If a precipitate is produced, it is collected on a filter and washed with water until free from chlorine. The filtrate is diluted, acidified with nitric acid, treated with a slight excess of standard silver nitrate solution, and then made up to a definite volume and filtered. The excess of silver in a measured portion of the filtrate is estimated by means of standard thiocyanate solution in presence of ferric alum. From the amount of hydrochloric acid thus found, the quantity of alkaloid can be calculated. In the case of brucine, the colour produced on adding the nitric acid interferes with the subsequent titration; a measured portion of the liquid is therefore evaporated to dryness on the water-bath, the residue ignited, and dissolved in hot dilute nitric acid, the solution being then titrated with thiocyanate. E. G.

Titration of Alkaloidal Salts. ERNST RUNNE (*Apoth. Zeit.*, 1909, **24**, 662—663; 1910, **25**, 137. Compare Kippenberger, Abstr., 1900, ii, 637; Astruc, Abstr., 1901, i, 604).—The results of an investigation into the possibility of titrating the acids of alkaloidal salts by standard alkali solutions, and the influence of various indicators on the results are given.

In solution in alcohol, morphine is slightly acid to Poirrier's blue, whilst quinine, cocaine, and codeine are neutral. In alcoholic solution, phenolphthalein is not reddened by any of these four alkaloids, but in aqueous solution, codeine is markedly alkaline, morphine and cocaine less so, whilst quinine is neutral to it. The alcoholic solution of each of the four alkaloids reddens, sooner or later, with phenolphthalein on dilution with water. A series of trials showed that quinine hydrochloride only may be titrated accurately in either alcohol or water, and with either of the two indicators, whilst quinine sulphate, cocaine hydrochloride, and codeine phosphate can only be titrated in alcohol or alcohol-water solutions with either indicator; morphine salts cannot be titrated accurately under any of the conditions tried. Poirrier's blue is on the whole the better of the two indicators for these purposes. T. A. H.

Chlorophyll Group. VI. The Estimation of Chlorophyll in Plants. HENRYK MALARSKI and LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1910, **24**, 319—322).—The chlorophyll is extracted and converted into chlorophyllan by means of acids, and the light absorption in chloroform solution is then quantitatively estimated by means of a König-Marten apparatus. As the absorption value of pure chloro-

phyllan is known, the amount of chlorophyllan obtainable from the plants under investigation can be readily calculated. The chlorophyllan values differ, however, in different plants, and even in the same plants grown under different conditions. S. B. S.

Estimation of Morphine. ERNST WINTERSTEIN (*Arch. exp. Path. Pharm.*, 1910, **62**, 139—144).—The method of Faust and Cloetta was adopted by Rübsamen in recent work on the estimation of morphine. Reasons are given in full to show that this method is not trustworthy. W. D. H.

Colour Reactions of Proteins. C. REICHARD (*Pharm. Zeit.*, 1910, **55**, 158—160, 167—168).—*Egg-Albumin.*—The tests are applied to the dried and powdered substance; when strongly pressed, the powder conglomerates. Sulphuric acid gives at first a colourless jelly, but on warming, a bluish-violet coloration appears; this again fades, but, after a few days' exposure to the air, a deep blue solution is formed, which gains in intensity by gently warming for some time. Fuming hydrochloric acid is well known as a test for proteins; but the author found that a weaker (25%) acid also gives a blue colour if the substance is evaporated with the acid, and then again re-moistened with it; the colour is not so permanent as with sulphuric acid. The test may be applied also by mixing the powder with a little sodium chloride and then moistening with sulphuric acid. Nitric acid gives at once an intense, yellow coloration, but a colourless 25% acid gives a colourless jelly, which, however, gradually turns sulphur-yellow; warming promotes the reaction. On adding strong alkali, the colour changes to a dark reddish-brown, but the yellow tinge is again restored on adding nitric acid. Glacial acetic acid is a good solvent for egg-albumin, and on evaporating the solution and gently drying the residue, a reddish-brown mass is obtained, which turns blue when moistened with sulphuric acid.

A somewhat similar coloration is obtained with trichloroacetic acid, whilst aminoacetic acid is without effect. A splendid reaction is obtained when an intimate mixture of the substance with ammonium heptamolybdate is moistened with sulphuric acid; the mixture turns almost black, but on exposure to the air an intense blue liquid is formed, which does not fade in the least. No reaction is obtained in the cold by substituting acetic acid or 25% hydrochloric acid for sulphuric acid, and this makes the test a very important one. If the substance is triturated with ammonium vanadate and a little water, the mass gradually turns an intense yellow; if a little 25% hydrochloric acid is added, a nondescript coloration is formed, which soon turns dark green and finally blue.

Several other tests are given (iodic acid, metallic salts, phenylhydrazine hydrochloride, picric acid, etc.), which are, however, less important. Attention is called to the behaviour of vanillin, which when mixed with the substance gives a splendid violet coloration on moistening with 25% hydrochloric acid; sulphuric acid may also be used, but acts somewhat more slowly. This reaction is a valuable one when testing for albumin in vegetable specimens under the microscope. L. DE K.

[Estimation of Proteins in Milk and Blood.] THEODOR WEYL (*Ber.*, 1910, **43**, 508—511).—See this vol., i, 287.

Medico-Legal Aspect of the Benzidine Reaction in the Examination of Blood Stains. FRÉD. BORDAS (*Compt. rend.*, 1910, **150**, 562—564. Compare Adler, Abstr., 1904, ii, 459).—It is stated that Adler's reaction, depending on the appearance of a coloration when blood is treated with hydrogen peroxide and benzidine, is not characteristic for blood, since pathological liquids, such as pus, and the juices of many fruit and plants, such as that of pears, spinach, and carrots amongst others, give the reaction equally well. Since the reaction is conditioned by the decomposition of hydrogen peroxide, it follows that any material capable of effecting this will develop a coloration with the reagent. This has been found to occur with many colloids, for example, ferrous oxalate solution and with pulverulent or porous substances, such as talc, pumice stone, alumina, and cellulose. In the case of blood, the reaction is produced by colloids, and as these are destroyed at 85°, McWeeny's method of applying the test (this vol., ii, 84) is useless. If, however, the catalytic activity of the blood is restored by contact with pure cellulose, the method is applicable even when the stained article examined has been washed in hot water. An imprint of the moist stain is made on filter paper which has been washed with acids until it no longer gives the reaction. A drop of hydrogen peroxide is then added, and followed by several drops of benzidine solution. The result, however, is only conclusive when the indication given is negative.

W. O. W.

Albert's Method of Determining Soil Acidity. H. SÜCHTING and TH. ARND (*Zeitsch. angew. Chem.*, 1910, **23**, 103—106. Compare *ibid.*, 1909, **22**, 533).—A number of determinations of acidity were made with different soils by the Tacke-Süchting method and by Albert's method (Abstr., 1909, ii, 446). The latter method gave very uncertain results, depending partly on the duration of the boiling, lower results being obtained by long boiling than by boiling for a shorter time.

It is pointed out that in employing the Tacke-Süchting method, the process must be carried out exactly as described.

N. H. J. M

[Albert's Method for Determining Soil Activity.] ROBERT ALBERT (*Zeitsch. angew. Chem.*, 1910, **23**, 106—107. Compare Abstr., 1909, ii, 446).—A reply to Süchting and Arnd (preceding abstract). Further experiments with different soils showed that in some cases the method is less exact than that employed by Tacke and Süchting. Satisfactory results were, however, obtained with different soils, by avoiding any great excess of ammonium salt and of baryta, the approximate amount of barium hydroxide required being first ascertained by adding baryta water to the soil suspended in water containing phenolphthalein. The results obtained by the modified method agree with those obtained by Tacke and Süchting's method.

N. H. J. M.

General and Physical Chemistry.

Specific Refractive Powers or Optical Constants of Substances in very Dilute Solutions. C. CHÉNEVEAU (*Compt. rend.*, 1910, **150**, 866—869. Compare Abstr., 1907, ii, 920).—Results of measurements by the interferential refractometer are given for dilute solutions of potassium chloride, ammonium nitrate, and magnesium nitrate. The conclusion drawn is that ionisation has no appreciable influence on the refractive power or "optical constant" of a substance in solution when the concentration exceeds 0·05%. W. O. W.

Refractive Index of Colloids. WALTER FREI (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 192—197).—The refractive index of dilute solutions of gelatin at 37° is found to be a linear function of the gelatin concentration. On addition of gradually increasing small quantities of sodium hydroxide to a 0·5% solution of gelatin at 22°, the refractive index is at first slightly increased, and then falls continuously. Neutral salts increase the refractive index of both acid and alkaline gelatin solutions. From observations made with different chlorides and sodium salts, the specific influence of various cations and anions has been determined.
H. M. D.

Determination of Constitution by Spectrochemical Methods. KARL AUWERS and FRITZ EISENLOHR (*Ber.*, 1910, **43**, 806—826).—As a result of refractometric measurements, Brühl has put forward certain rules with respect to the optical behaviour of unsaturated compounds (compare Trans., 1907, **91**, 115). These rules permit not only of the determination of the degree of unsaturation of such compounds, but can also be used to decide whether conjugated double linkings are present or not. In the literature, however, there are numerous examples of compounds which do not conform to Brühl's rules. This want of conformity may be real, or it may be due to the substances investigated being impure, and the authors have commenced an extended investigation on the subject.

A conjugated double linking should give rise to optical exaltation. If the molecular refractivities are taken for comparison, any small error in the atomic refractivities of the atoms of a compound may give rise to serious errors in the molecular refractivity in the case of compounds of high molecular weight. The authors, therefore, recommend that the "*specific refractivity* × 100," which they denote by Σ_a, or Σ_D, should be used for purposes of comparison. When this is done, apparent anomalies which exist in certain homologous phenol ethers (anisole, phenetole, etc.) when their molecular refractivities are compared are done away with.

Optical exaltation is taken as existing when the experimental value for Σ is greater than the theoretical by 0·30—0·35. In the case of specific dispersion, there is an exaltation when the deviation from the

theoretical value for $\Sigma_\gamma - \Sigma_\alpha$ amounts to 0·12—0·15, or when the deviation from the theoretical molecular dispersion amounts to more than 12—15%.

As far as the authors' experiments go, abnormally high molecular refractivities are obtained with only two groups of compounds which do not possess conjugated double linkings, namely, with methylene derivatives, $>C{:}C<$, containing a semicyclic double linking, and with compounds containing a 3-ring of carbon atoms. The exaltation is especially marked when a 3-ring is conjugate with a double linking.

The addition of side-chains to the central carbon atom of a conjugated system lowers the optical effect of the latter. The greater the number of such side-chains the less optically abnormal become the compounds. Thus the exalting effect of conjugated systems diminishes in the order:

$$\text{I.}\ \cdot CH{:}CH\cdot CH{:}CH\cdot \longrightarrow \cdot CH{:}\underset{R}{C}\cdot CH{:}CH\cdot \longrightarrow \cdot CH{:}\underset{R}{C}\cdot\underset{R^{I}}{C}{:}CH$$

$$\text{II.}\ \cdot CH{:}CH\cdot CH{:}O \begin{array}{c}\nearrow \cdot CH{:}CH\cdot\underset{R}{C}{:}O \searrow \\ \searrow \cdot CH{:}\underset{R^{I}}{C}\cdot CH{:}O \nearrow\end{array} \cdot CH{:}\underset{R^{I}}{C}-\underset{R}{C}{:}O$$

Ring formation in a conjugated system acts similarly to the addition of a side-chain. Thus the cyclic compounds of the type $\genfrac{}{}{0pt}{}{-C}{-C}{>}C\cdot\underset{R}{C}{:}CH$ and $\genfrac{}{}{0pt}{}{-C}{-C}{>}C\cdot\underset{R}{C}{:}O$ correspond in their optical behaviour with the acyclic compounds of the type $\cdot CH{:}\underset{CH_3}{C}-\underset{R}{C}{:}CH$ and $\cdot CH{:}\underset{CH_3}{C}-\underset{R}{C}{:}O$.

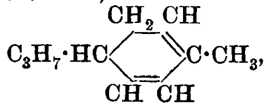
A system of conjugated double linkings which has been altered by substitution in any of the above ways is called a "*disturbed conjugation*," and one may speak of "*undisturbed*," "*simply disturbed*," and "*much disturbed*" conjugations.

Substitution at the end carbon atoms of a conjugation may diminish the optical exaltation. Such *lateral* disturbances are especially marked when there is already a *central* disturbance in the conjugated system, and in some cases the exaltation may be completely eliminated. Thus systems such as $\cdot\underset{R}{C}{=}\underset{R^{I}}{C}-\underset{R^{II}}{C}{:}O$ and $\cdot\underset{R}{C}{=}\underset{R}{C}-\underset{R^{II}}{C}{=}\underset{R^{III}}{C}\cdot$ show very little exaltation.

Different side-chains have different effects. An alkyloxy-group, such as OCH_3 or OC_2H_5, lowers the exalting effect of a conjugation much less than a hydroxyl or alkyl group.

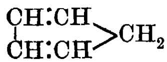
The above regularities show why α-phellandrene, which according

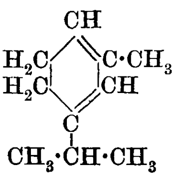
to Wallach (Abstr., 1904, i, 1035) has the constitution



is optically normal; it possesses a disturbed conjugation.

The influence of disturbed conjugations is also marked when the disturbing substituent also contains a double linking, and by its entrance into the molecule increases the number of conjugations. Compounds which contain a series of three double linkings, as CH⁚C·C⁚C·C⁚C· and CH⁚C·C⁚C·C⁚O, possess a very high refractivity and dispersivity. If, however, the three double linkings are crossed, the exaltation is very much diminished, and becomes even less than that of the parent substance with only two conjugations. This explains why methyl 1 : 4-dimethyl-$\Delta^{1,3}$-*cyclo*hexadiene-2-carboxylate (Abstr., 1908, i, 520) does not exhibit the usual exaltation.

In all cases the dispersivity is strongly exalted when the refractivity shows only a slight exaltation. In some cases where an exaltation of the refractivity is to be expected, there is a depression instead. This may be due to impurity of the compound, or to polymerisation. The latter cause accounts for the abnormal results obtained with *cyclo*pentadiene,  (Abstr., 1896, i, 289). Although this compound shows a depression of the molecular refractivity, the molecular dispersivity is exalted above the theoretical by 115%.

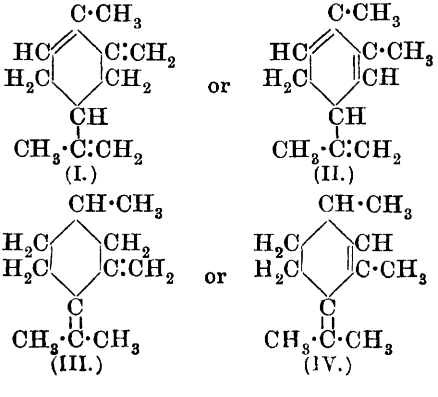


The above results may be applied to determining the position of the ethylene linking, and the authors consider that Fisher and Perkin's formula for *iso*carvestrene (Trans., 1908, 93, 1890) should be replaced by the annexed formula.

T. S. P.

Determination of Constitution by the Optical Method.

Karl Auwers and Fritz Eisenlohr (*Ber.*, 1910, 43, 827—834).—The rules deduced in a former paper (see preceding abstract) are applied in various cases, the optical constants being redetermined by the authors.



Methylmenthatriene (Abstr., 1907, i, 597; 1908, i, 433) must possess either the formula (I) or (II), the molecular refractivity and dispersivity being slightly exalted, owing to the doubly disturbed conjugation. It is not possible to decide between these two formulæ

on optical grounds. Other formulæ which have been proposed would necessitate either a very high exaltation or else a normal refractivity and dispersivity. Similar results show that the compound resulting from the interaction of magnesium methyl iodide and pulegone (Abstr., 1908, i, 556) has either the formula (III) or (IV).

The compound resulting from the action of zinc chloride on methylheptenone (Abstr., 1907, i, 597) possesses optical properties corresponding with 1 : 3-dimethyl-$\Delta^{1,3}$-*cyclo*hexadiene. T. S. P.

Magnetic and Electrical Double Refraction of Aromatic Liquids and the Theory of Molecular Orientation. A. Cotton and Henri Mouton (*Compt. rend.*, 1910, **150**, 774—777. Compare Abstr., 1909, ii, 773).—The magnetic and electrical double refraction of aromatic liquid substances both diminish as the temperature rises, but the rate of diminution is considerably greater in the case of the electrical effect. If the values obtained for the electrical double refraction of nitrobenzene at different temperatures are divided by the corresponding values of the dielectric constant, numbers are obtained which vary with the temperature at approximately the same rate as the magnetic double refraction. This relationship is cited as evidence in support of the theory that the double refraction effects are due to orientation of the molecules in the magnetic and electrical fields. The fact that the dependence of the double refraction on the wave-length follows the same law for different substances is supposed to indicate that the action is due to the same cause in all cases. H. M. D.

Effect of Pressure on Arc Spectra: Titanium. R. Rossi (*Proc. Roy. Soc.*, 1910, **83**, *A*, 414—420).—The spectrum was obtained from an arc burning between a negative carbon rod and a positive pole consisting of a graphite tube filled with powdered titanium carbide. The arc thus obtained was found to burn under pressure far better than an arc between metallic poles. Pressures up to 100 atmospheres were used. All the lines examined were found to be broadened by pressure, the amount and the nature of the broadening being different, however, for different lines. Numbers representing the observed displacements of fifty-two lines at 15, 30, 50, and 100 atmospheres are recorded. As mean displacement per atmosphere the value 0·00365 Ångström unit was obtained. Some lines are found to have the same relative intensities at the different pressures examined, but the majority undergo a change. H. M. D.

Extension of Band Spectrum of Nitrogen in Extreme Red and Infra-red. F. Croze (*Compt. rend.*, 1910, **150**, 860—863).—Two new series, each consisting of eight bands, more refrangible than those hitherto recorded, have been observed in the spectrum of nitrogen. The two most refrangible of the new bands belong to the fifth sub-group, whilst the next six constitute a sixth sub-group. The wave-lengths of the new bands are given, and the numbers shown to be in good agreement with those calculated from Deslandres' formula (Abstr., 1902, ii, 373). W. O. W.

Measurement of Normal Lines in the Helium Spectrum. P. EVERSHEIM (*Zeitsch. wiss. Photochem.*, 1910, **8**, 148—150).—The interferometer method used by the author for the measurement of standard lines in the iron spectrum has been applied to the determination of the wave-lengths of seven lines in the helium spectrum. The lines in question can be measured with great precision, and are recommended as very suitable for calibration and comparison purposes.

H. M. D.

The Spark Spectra of Potassium and Sodium. R. SCHILLINGER (*Wien. Sitzungsber Akad. Wiss.*, 1909, **118**, 604—627).—The paper contains a detailed account of the author's experiments on the spark spectra of sodium and potassium in an atmosphere of hydrogen. A Rowland concave grating of high dispersion was employed; an Ångström unit corresponded in the primary spectrum with about 0·38 mm. The portions of the spectrum examined consisted of lines from λ 7700 in the red to λ 2100 in the ultra-violet, the wave-lengths measured being tabulated comparatively with the results of other workers. The plates employed were exposed during two to six hours in the ultra-violet, and for seventy hours in the lowest part of the red. A comprehensive bibliography is also appended.

F. M. G. M.

Light Emission and its Excitation. PHILIPP LENARD (*Ann. Physik,* 1910, [iv], **31**, 641—685. Compare Abstr., 1905, ii, 565). —A detailed investigation has been made of the bands in the phosphorescence spectra of the alkaline earth metal and zinc sulphides. In particular, the connexion between the wave-length of the exciting light and the intensity of the excited phosphorescent light has been examined. The observations indicate that three types of phosphorescent light emission can be distinguished. Two of these are characterised respectively by relatively slow and very rapid rays of decay, whilst the third is only excited to any considerable extent by ultra-violet radiations. The processes which give rise to the three types of emission are shown to be independent of one another.

An explanation of the observations is put forward in terms of the theory of electrons. H. M. D.

Dispersion and Absorption of Metals for the Visible and Ultra-violet Spectrum. WILLI MEIER (*Ann. Physik,* 1910, [iv], **31**, 1017—1049).—From observations on the reflexion of light at metallic surfaces, the author has obtained values for the refractive index and the coefficient of absorption. The substances investigated were gold, nickel, iron, platinum, bismuth, zinc, selenium, mercury, a 50% alloy of copper and silver, Wood's metal, and iodine. The indices of refraction and of absorption are recorded in each case for a series of wave-lengths.

It is shown that in all cases the dispersion agrees with that required by Drude's theory if the assumption is made that bound, as well as free, electrons take part in the influence exerted by the reflecting substances on the incident rays. H. M. D.

Absorption Spectra of Vapours of the Alkali Metals. P. V. BEVAN (*Proc. Roy. Soc.*, 1910, **83**, *A*, 421—428. Compare this vol., ii, 87).—The absorption spectra of the vapours of rubidium and cæsium have been examined by the method already used by the author in the case of potassium. The vapours were obtained by heating the chlorides with sodium or potassium. This method is found to give vapours which contain sufficient rubidium or cæsium to yield well-developed absorption spectra. The spectra obtained show twenty new lines in the case of rubidium and eleven in that of cæsium, bringing up the number of principal series lines to twenty-five and twenty-one respectively.

The measured wave-lengths of the principal series lines of sodium, potassium, rubidium, and cæsium have been used to test the various formulæ which have been suggested for expressing the connexion between them. Ritz's equation is found to give better results than the formula of Kayser and Runge, or that of Rydberg, but it does not agree well enough with the observations to be regarded as anything more than an empirical formula. H. M. D.

Absorption Spectra of Certain Uranous and Uranyl Compounds. HARRY C. JONES and W. W. STRONG (*Phil. Mag.*, 1910, [vi], **19**, 566—572).—An account of work previously published (compare this vol., ii, 87, 172, 247). H. M. D.

Optical Investigation of the Chromophores of Coloured Salts and Acids. ARTHUR HANTZSCH (*Zeitsch. physikal. Chem.*, 1910, **72**, 362—380).—The observation that the ionised and non-ionised components of coloured salts with saturated complexes are optically identical is confirmed by further examples (compare Hantzsch and Clark, Abstr., 1908, ii, 447, 646). Deviations from Beer's law are due to chemical changes of the coloured complexes. Alkaline chromate solutions contain only CrO_4'' ions, and follow Beer's law. Acid chromate solutions contain mainly Cr_2O_7'' ions, but also Cr_3O_{10}'' ions in amount increasing with the acid concentration, and this chemical change accounts for the non-validity of Beer's law in this case.

Complexes such as CrO_4, Cr_2O_7, MnO_4, and $Co(NH_3)_2(NO_2)_4$, are optically constant even at 100° in the absence of decomposition; others, such as $PtCl_6$ and $Fe(CN)_6$, show a slight, and copper sulphate a very considerable temperature-coefficient. Solvents diminish slightly the light-absorbing power of coloured complexes, the effect being an almost parallel displacement of the absorption for different substances, as in the case of the temperature.

Attempts were made to compare the absorption of solid salts with that of their saturated solutions, but the results were only satisfactory in the case of copper sulphate, where the solid and solution are optically identical. It is probable that the solid salt has the formula $Cu(OH_2)_4SO_4,H_2O$, and the alteration of this hydrated complex with rise of temperature would account for the observations in aqueous solution. Solid potassium ferrocyanide appears to absorb light considerably less strongly than does its aqueous solution. G. S.

Luminescence. III. Deviations from Stokes' Law. JOSEPH DE KOWALSKI (*Bull. Acad. Sci. Cracow*, 1910, *A*, 12—16).—In order to account for the behaviour of fluorescent substances which deviate from the requirements of Stokes' law, the author assumes that the difference between the energy of the liberated electrons and that of the existing light is derived from the kinetic energy of molecular movement. Experiments were made to ascertain whether the emitted luminescent energy is altered when the thermal energy of the molecules is changed by an alteration in the temperature of the fluorescent substance.

For this purpose very dilute solutions of rhodamine in ethyl alcohol were submitted to the action of yellow light of wave-length $\lambda = 577\ \mu\mu$ at room temperature and at $-185°$. Whereas at room temperature the limit of the fluorescent spectrum appeared to be at $\lambda = 557\ \mu\mu$, this was shifted to $\lambda = 565\ \mu\mu$ at $-185°$. This result is in agreement with the view that a portion of the energy of the electrons is derived from the energy of molecular motion.

The relationship between the limiting wave-lengths of the fluorescent spectrum and the corresponding temperatures is shown to be in accordance with the requirements of the Planck-Einstein light quantity theory. H. M. D.

Luminescence. IV. Absorption and Phosphorescence of Certain Organic Compounds. JOSEPH DE KOWALSKI (*Bull. Acad. Sci. Cracow*, 1910, *A*, 17—22. Compare preceding abstract).—Spectrographic measurements have been made of the phosphorescence spectra of benzene, toluene, ethylbenzene and *p*-xylene in 0·05 molar solution in ethyl alcohol. The spectra consist of a series of bands on a continuous back-ground. The rate of decay of the continuous spectrum is very much greater than that of the banded spectrum. When the oscillation frequencies corresponding with the bands in the phosphorescent spectrum are compared with those of the bands in the absorption spectra, a nearly constant difference is obtained in the case of each hydrocarbon. From this the author draws the conclusion that for each absorption band there is a corresponding phosphorescence band, the frequency of which differs from that of the absorption band by a constant amount. H. M. D.

Phosphorescence of Uranyl Salts at very Low Temperatures. HENRI BECQUEREL, JEAN BECQUEREL, and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, **150**, 647—652. Compare Abstr., 1886, 189; 1896, ii, 406; 1907, ii, 213; 1908, ii, 243, 338; 1909, ii, 630).—A résumé and discussion of work already published. W. O. W.

Polarisation Phenomena in Liquid Crystals of Cholesterol Ester. FRIEDRICH GIESEL (*Physikal. Zeitsch.*, 1910, **11**, 192—193).—An examination of the light reflected from, and transmitted by, an iridescent supercooled mixture of cholesterol esters has shown that the reflected and transmitted rays are circularly polarised in opposite directions. H. M. D.

Rotatory Power of Coloured Solutions. III. Rotation Dispersion of Certain Coloured Complex Tartrates. HERMANN GROSSMANN and ALBERT LOEB (*Zeitsch. physikal. Chem.*, 1910, 72, 93—112. Compare Abstr., 1906, ii, 823; *Zeitsch. Ver. deut. Zuckerind*, 1908, 994).—The solutions were prepared by adding to a constant amount of tartaric acid varying amounts of the metallic salt and of alkali hydroxide, and making up to 20 c.c. in each case. In order to determine the dispersion in such solutions, the rotatory power was measured for red (*r*), green (*g*), yellow (*D*), and light blue (*lb*), light.

In solutions containing uranyl nitrate and sodium hydroxide, the maximum rotation occurs when at least 1 mol. of the uranyl salt and 3 mols. of the alkali are present for every mol. of tartaric acid. The dispersion appears to be normal. The presence of tartaric acid does not prevent the precipitation of uranium salts by sodium hydroxide.

Solutions of tartaric acid to which a cobalt salt and alkali hydroxide in excess have been added are moderately stable in concentrated solution, but very unstable in dilute solution; from the latter solutions brown cobalt hydroxide soon separates. In red light the gradual addition of alkali to the acid solution of the cobalt salt causes a change in the sign of the rotation (from positive to negative) before the solution is alkaline, whilst $[\alpha]_{lb}$ is always positive, even in alkaline solution. Mutarotation was observed only in alkaline solution; in dilute solution, $[\alpha]_r$ and $[\alpha]_D$, which are towards the left, diminish with time, and $[\alpha]_{lb}$, which is towards the right, also diminishes when the solution is kept. Although tartaric acid does not prevent the precipitation of cobalt hydroxide by alkali hydroxides, a solution containing a large excess of sodium carbonate instead of the hydroxide remains clear.

In contrast to cobalt salts, very dilute alkaline solutions containing 4 atoms of nickel to 1 mol. of tartaric acid remain clear. When the solutions are just alkaline, they are strongly dextrorotatory. As the amount of alkali is gradually increased, the rotation first diminishes, reaches a minimum, and then increases. The dispersion is normal.

When sufficient tartaric acid is present, neither sodium hydroxide nor carbonate nor ammonium hydroxide precipitate aluminium hydroxide from solutions of aluminium salts. The addition of sodium hydroxide to a solution containing 2 mols. of tartaric acid and 1 mol. of aluminium nitrate increases the specific rotation, which attains a maximum before the solution has become alkaline, and a second maximum in alkaline solution; these solutions possess the highest specific rotation. The results indicate that the complexes present in such solutions contain 2 mols. of tartaric acid to 1 atom of aluminium. The dispersion of these solutions is normal.

Solutions containing ferric salts behave somewhat like those containing aluminium, inasmuch as those containing 2 mols. of tartaric acid to 1 atom of iron are stable in the presence of excess of alkali. The same is true, however, of solutions containing 1 mol. of the acid to 1 atom of iron, and the latter show the highest rotation. Solutions containing 2 atoms of iron to 1 mol. of tartaric acid are

immediately precipitated by the addition of alkali. In general, the specific rotation of all these solutions tends to diminish with increase in the amount of alkali. The results appear to indicate the existence of several complexes in these solutions.

A few experiments in which mannitol was used instead of tartaric acid are also described. Alkaline solutions containing mannitol and chromic salts show anomalous dispersion (compare Cotton, *Ann. Chim. Phys.*, 1896, [iv], 8, 406). G. S.

Photochemical Equilibria. IV. Photochemical Equilibrium of Water Vapour. ALFRED COEHN (*Ber.*, 1910, 43, 880—884. Compare this vol., ii, 173).—Using an arrangement similar to that described in previous papers, the authors find that under the action of ultra-violet light at 150°, hydrogen and oxygen combine almost completely, with the formation of water vapour. Although combination takes place with considerable velocity, there is no explosion. At the same temperature, water vapour is decomposed by ultra-violet light to a very slight extent, the minimum decomposition found being 0 00087—0·0010%. This amount of decomposition is the same as the thermal decomposition existing at about 1250°, so that the equilibrium under the influence of ultra-violet light is different from the ordinary thermal equilibrium. T. S. P.

Solarisation in Aqueous Solution. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1910, 8, 135—148. Compare Abstr., this vol., ii, 115).—If solutions containing ammonium oxalate and a small quantity of a ferric salt are exposed to light and then treated with excess of ammoniacal silver nitrate solution, the quantities of ferrous salt, which are indicated by the amounts of precipitated silver, are found to increase continuously with the period of insolation. When, however, instead of ammoniacal silver solution, mercuric chloride is added as developer, it is found that the amount of mercurous chloride precipitated increases with the period of insolation of the oxalate solution until a maximum is reached; for longer exposures the quantity of mercurous salt gradually diminishes. This phenomenon is considered to be analogous to that of photographic solarisation. If the insolated solutions contain oxygen, the quantities of mercurous chloride obtained after short exposures are abnormally small. This induction period is caused by the rapid oxidation of the ferrous oxalate by the dissolved oxygen. In the absence of oxygen there is no evidence of an induction interval. H. M. D.

Chemical Action of Light. VI. Photochemical Phenomena in Dye Solutions. FRITZ WEIGERT (*Ber.*, 1910, 43, 951—955. Compare this vol., ii, 174; Gebhard, *ibid.*, ii, 248).—It is shown that the increase of pressure observed when a solution of uranin, in contact with oxygen or air, is exposed to light is due, at least partly, to the liberation of carbon dioxide. The accelerating influence of the alkali in Gebhard's experiments may be due, therefore, to a diminution of the partial pressure of the carbon dioxide. C. S.

Biological Radioactivity. ANDRÉ LANCIEN and LOUIS THOMAS (*Chem. Zentr.*, 1909, ii, 1958; from *Bull. Sci. Pharm.*, 1909, 16, 590—597).—Investigations were made to determine whether plants and animals were capable of ionising gases. The results were negative. Animals into which radioactive salts had been injected proved to be radioactive. S. B. S.

The Disintegration Products of Radium and Thorium in the Atmosphere. DOMENICO PACINI (*Physikal. Zeitsch.*, 1910, 11, 227).—The paper contains a table of twenty-two tests on the rendering active of negatively-charged wires exposed to the atmosphere, with full details of the conditions of the experiments and of the meteorological conditions prevailing. The tests were made at the Sestola Observatory in the Apennines, 1090 metres above the sea, a position chosen as being open to the wind in nearly all quarters. Exposures were made for four hours, in which time the radium products attain equilibrium, and from the curve of decay of the activity, the ratio of the number of atoms of radium emanation to that of thorium emanation in the air was calculated. The mean value of this ratio was 6700. Light winds from the plains and valleys, during or two hours before the test, increased the ratio, while with falling barometer and strengthening winds from the same quarter, the ratio decreased. Wind from the high mountains increased the ratio. The time taken for half the initial activity to decay in seventeen out of the twenty-two observations varied from fifty-six to sixty-five minutes. The smallest value was fifty-two minutes, corresponding with 29%, and the largest value was eighty-five minutes, corresponding with 73% of the initial activity being due to thorium. F. S.

The Measurement of the Constant of the Radium Emanation. Mme. MARIE CURIE (*Le Radium*, 1910, 7, 32).—New measurements have been made of the rate of decay of the activity of the radium emanation, both by P. Curie's original method, using a sealed tube of emanation and measuring the penetrating rays only, and also by enclosing the emanation in an air-tight ionisation vessel and measuring the total radiation. The values agree in ten experiments, five by each method, to within 1%, and the value of the period of half-change, 3·85 days, is deduced. This agrees with that of Sackur, 3·86 days, and of Bumstead and Wheeler, 3·88 days, and is exactly midway between the two original values of 3·71 days (Rutherford and Soddy) and 3·99 days (P. Curie). The period of average life is therefore 5 55 days, and the value of the radioactive constant is 0·00751 $(\text{hour})^{-1}$. A similar value was obtained by the regeneration of penetrating rays from a salt of radium, kept in a sealed tube, which had initially been deprived of emanation. The exponential decay at the rate given has been proved to hold over a period of three months, during which time the concentration of the emanation diminishes more than 10^7 times, and in different experiments for concentrations differing by 2×10^{11} times, so that concentration has no effect on the rate of change. Between three and twenty hours after the admission of emanation, the rate of decay appeared to be slightly less than normal, and to increase

more and more quickly, until after twenty hours the normal rate was attained, but it was difficult to establish beyond doubt such a real variation in the constant. Tables of the decay and recovery of the radium emanation with the values for the constant here given have been drawn up by Kolowrat (*Le Radium*, 1909, 6, 193). F. S.

The Photographic Action of α-Particles Emitted from Radioactive Substances. S. Kinoshita (*Proc. Roy. Soc.*, 1910, *A*, 83, 432—453).—The number of grains in a developed photographic film, darkened by exposure to α-rays, as counted under the microscope, depends only on the number of particles falling on the film. The size of the grains does not depend on the latter, but increases with time of development to a definite limit. This well explains the peculiarity, here experimentally established, that the photographic action of the α-rays along its path is constant almost up to the end of the range, and does not show the increase, as the range increases, which is the case for the ionisation. The halide grains, whether strongly or weakly ionised by the α-ray at different points of its path, all develop up to the same limit when development is complete. It is deduced from a study of the variation of density of the film, as measured by a König's spectrophotometer, with the (known) number of α-particles per sq. cm. allowed to act on it, that a halide grain may be changed and rendered capable of development when struck by a single α-particle. The numbers of α-particles actually obtained by so counting the grains may be more or less than the real number according to the nature of the plate, and whether each α-particle strikes more than one grain, or whether some pass through without striking a grain, but the number found for two different kinds of plates did not vary much from the actual number. It is indicated that α-particles could be counted by the photographic method with accuracy if an emulsion of very fine halide grains, such that no α-particles could pass through without striking a grain, could be prepared, and a very high magnification employed. F. S.

Absorption of β-Rays from Radium by Solutions and Liquids. W. A. Borodowsky (*Phil. Mag.*, 1910, [vi], 19, 605—619).—It was found that two separate liquids together absorbed the β-rays of radium to the same extent as after mixing, the thickness of the liquid layer being unchanged, although the two liquids may react chemically on mixture, as, for example, solutions of silver sulphate and barium chloride. The results throughout with liquids are expressed in terms of aluminium, the thickness of the latter required to reduce the radiation to the same degree as a definite depth of solution being determined. The liquids were always contained between two surfaces of thin glass, and the results of Allen (*Physical Review*, 1909, 29, 177) are ascribed to imperfect methods of experiment. It was found that solutions absorb β-radiation according to the same law as solids, the absorption of the solution being directly proportional to the mass of salt present. The absorption of compounds follows an additive law, the relative absorption depending on the nature of the atoms themselves, but not on their arrangement within the molecule.

F. S.

The Experimental Testing of the Question of the Nature of the γ-Rays. EGON R. VON SCHWEIDLER (*Physikal. Zeitsch.*, 1910, **11**, 225).—The paper discusses theoretically the possible ways of experimentally distinguishing between the two rival theories of the nature of the γ-rays, the older ether-impulse theory and the newer corpuscular theory. If γ-rays from a point source pass through a hole in a distant opaque screen, on the first theory variation of the size of the hole will not vary the number of γ-rays contributing to the effect on the far side of the screen, whereas on the second theory the number of γ-rays involved is diminished proportionally to the area of the aperture. The von Schweidler variation of radioactive change, being inversely proportional to the square root of the number of rays expelled, or of atoms disintegrating, per unit of time, should therefore give the means of distinguishing between the two theories. Experiments are in progress. It is claimed that by means of a differential method, due to K. W. F. Kohlrausch, such variations in the γ-rays have been detected. F. S.

Long-period Determination of the Rate of Production of Helium from Radium. Sir JAMES DEWAR (*Proc. Roy. Soc.*, 1910, *A*, **83**, 404—408. Compare Abstr., 1908, ii, 921).—The amount of helium formed in the 70 mg. of radium chloride, before used, after it had been kept sealed up for nine months, was determined by breaking off the end of the tube (after it had previously been thoroughly heated to expel the helium), and thereby putting it into connexion with an exhausted McLeod gauge of known volume, having a charcoal bulb, cooled in liquid air, attached for absorbing adventitious gases. This was accomplished by an ingenious device fully described. The rate of production found was 0·463 cu. mm. of helium per gram of radium per day. The value previously given (0·37 cu. mm.) was erroneously estimated, and should have been 0·499, and the true value is considered to be probably between 0·463 and 0·499. F. S.

Gases Containing Helium from the German Salt-beds. ERNST ERDMANN (*Ber.*, 1910, **43**, 777—782).—In August, 1904, 450 metres underground in the Herzogl. Salz-werk at Leopoldshall, a jet of inflammable gas broke out through a hole blasted in the carnallite bed, which burnt at first with a flame 1 metre long, and has continued four and a-half years at gradually decreasing pressure, many hundred thousand cubic metres of gas having escaped. Analysis of this gas showed 83·6% hydrogen, 4·4% marsh gas, and an inert residue of 12%; oxygen, carbon monoxide, and dioxide, ethylene and acetylene being absent. In the residue a considerable amount of helium, with a detectable quantity of neon, is present. A minimum estimate gives the proportion of rare gas as 0·17 volume % of the natural gas, so that a total of at least 12 cubic metres of rare gas must have escaped in the four and a-half years. The origin of hydrogen in carnallite is unexplained. Precht has attributed it to the action of steam on the ferrous chloride in carnallite. Rinnite

$(FeCl_2,3KCl,NaCl)$,

both natural and artificial, heated with water in exhausted sealed

tubes to 100—110°, was, however, found to give no trace of hydrogen. The presence of a radioactive impurity in the carnallite would explain, not only (1) the presence of helium, but also (2) the far greater quantity of hydrogen, from the radioactive decomposition of water, the oxygen oxidising the iron as in Precht's theory, and (3) the well-known occurrence of blue rock-salt (through the action of radium rays on sodium chloride). In an addendum, Strutt's work on helium in carnallite (Abstr., 1908, ii, 923) is referred to, and the previously expressed opinion is preferred, that radioactive admixtures with the carnallite rather than the radioactivity of potassium itself is the cause of the phenomena. F. S.

Distribution of Photo-electric Cathode Rays in a Vacuum and in Different Gases. James Robinson (*Ann. Physik*, 1910, [iv], **31**, 769—822).—The first part of the paper deals with experiments which were made to ascertain the mode of distribution of the electrons emitted in a vacuum by a metal plate subjected to ultraviolet radiation. The number of electrons emitted in any particular direction is a function of the angle which this makes with the direction of the incident rays. As the angular separation increases, the electron emission diminishes considerably, but it seems possible that some electrons are even emitted at 90° to the direction of incidence.

Measurements were also made of the absorption of cathode rays of widely different velocities in various gases. With diminishing velocity, the absorption increases to a limiting value, which is unaltered by further reduction of the velocity. In comparison with oxygen, nitrogen, and carbon monoxide, the behaviour of hydrogen is abnormal. For high speed cathode rays, the absorption of hydrogen is smaller than that of the other gases, but for rays of small velocity, the relative absorptive powers are reversed.

From the values of the absorption for low speed electrons, the author calculates the diameters of the molecules of the various gases investigated. H. M. D.

The Chemical Decomposition of Water by the α-Rays of Polonium. K. Bergwitz (*Physikal. Zeitsch.*, 1910, **11**, 273—275. Compare Curie and Debierne, this vol., ii, 251; Rutherford and Boltwood, this vol., ii, 175).—A piece of copper foil covered with an extremely active deposit of polonium, prepared by Giesel, was immersed in water in a small burette, and the evolution of gas measured. In two hundred and forty hours, about 0·5 c.c. of hydrogen and 0·05 c.c. of oxygen were collected, and in a further ninety-six hours, about 0·18 c.c. of hydrogen and 0·022 c.c. of oxygen. Allowing for the gases dissolved in water (0·10 c.c. of hydrogen and 0·18 c.c. of oxygen in the first experiment), a total of 0·825 c.c. of mixed gas, in the ratio of 2·5 of hydrogen to 1 of oxygen, was collected. In the second experiment, the ratio was 2·1 : 1. Peroxide of hydrogen was not detected. By indirect calculations of the number of α-particles expelled, from the saturation ionisation current of the polonium, and of the energy absorbed in the production of the

observed volume of gas, it is deduced that 10% of the energy of the α-particles is used in producing chemical decomposition.

F. S.

The Radioactivity of Potassium. JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1910, 11, 275—280).—In a general discussion of the radioactivity of potassium, experiments, with negative results, are described having for their object, firstly, the concentration of an impurity or constituent responsible for the radio activity, and, secondly, the detection of a potassium emanation by means of an active deposit. In some cases, large amounts of material were worked up in the Kgl. Kali-werk at Vienenberg am Harz. It had been noticed in 1905, in investigations of the penetrating rays from the earth's crust, that whereas the latter over the thick rock-salt deposits at Hedwigsburg, near Wolfenbuttel, was, as is to be expected, abnormally low, as soon as the rock-salt layers gave place to the carnallite beds, a clear rise in the intensity of the penetrating rays occurred, and this the authors are now inclined to explain as due to a specific activity of the potassium in carnallite. With regard to the first object of the work, electrolysis of potassium chloride with mercury cathode, fractional precipitation of potassium by hydrofluosilicic acid, and digestion of solutions of potassium salts with bone-charcoal and colloidal sulphur, all failed to give any active product. The attempts to obtain a potassium active deposit were carried out in the carnallite mine itself by stretching a negatively charged wire across a boarded up space in the carnallite layer 10 metres high for several hours. No certain evidence of a special active deposit was obtained, and the conclusion is drawn that the activities of potassium and rubidium are most probably due to the elements themselves, not to impurities. F. S.

The Passage of β-Rays through Matter. II. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1910, 11, 262—273. Compare this vol., ii, 7).—The paper is chiefly concerned with the absorption of the β-rays of uranium-*X* by liquids (for holding which a special micrometer-screw cell, in which the thickness of the layer of liquid can be varied, is described) and with the comparison of the results obtained with theoretical expressions, deduced by the author in numerous preceding papers, on the further assumption that the action of the component atoms of the molecule is purely additive. The general result is in good agreement with the theoretical expressions, the passage of the β-rays through matter being wholly independent of the nature of the substance, and depending only on two constants, experimentally determinable for each type of β-ray, and the atomic weights of the atoms contained in the substance. Light substances tend to absorb somewhat less, and heavy substances somewhat more, than the theory indicates. The first part of the paper is concerned with a discussion of the effect of different experimental dispositions on the absorption, and the latter part with the results of S. J. Allen (*Physical Review*, 1909, 29, 177) in a similar field with the β-rays of radium, which are shown to agree for the most part with the author's theory. F. S.

Coloured Hydrides of the Alkali Metals and their Photo-electric Sensitiveness. JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1910, 11, 257—262).—The sensitiveness of photo-electric cells with cathode of alkali metal varies considerably in different cells apparently exactly similar, even when the surface of the metal, such as the liquid alloy of sodium and potassium, is perfectly free from contamination. Often the sensitiveness is increased, and the brilliancy of the surface at the same time impaired, by passing a glow discharge through the cell. These differences have been traced to the presence of hydrogen. When the alkali metal is completely converted into colourless hydride, no photo-electric sensitiveness is shown. By subjecting this colourless hydride to the action of cathode rays, just as in the case of the halogen compounds (Goldstein), characteristic, more or less transient, and unstable coloured products result (bluish-violet for potassium, similar but paler for rubidium, slightly green for cæsium, and brownish-yellow for sodium), with evolution of hydrogen and production of photo-electric sensitiveness to the visible region of the spectrum. By causing, as in Mey's method, hydrogen to be absorbed by the pure alkali metal in the cold under the action of the glow-discharge, the photo-electric sensitiveness of the cell is increased three or four times. Nitrogen is without action. The intensely coloured compounds are regarded as solid solutions of colloidal alkali metal in excess of undecomposed compound, and the photo-electric property appears to be bound up with the existence of this condition. F. S.

Photo-electric Sensitiveness of the Alkali Metals as a Function of the Wave-length. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1910, 215—228).—Experiments are described which show that the variation of the photo-electric sensitiveness of potassium sodium alloy with the wave-length of the existing light is dependent on the angle which the incident beam makes with the surface of the metallic alloy. For perpendicular incidence, the photo-electric sensitiveness increases continuously as the wave-length of the exciting beam diminishes. When, however, the angle of incidence differs from zero, the sensitiveness exhibits a maximum for rays within the region of the visible spectrum. This is due to the fact that the ratio between the amount of absorbed light and the photo-electric effect for the vector component which lies in the plane of incidence is a function of the wave-length of the incident radiation. The results obtained furnish a satisfactory explanation of the apparently discrepant results obtained by Elster and Geitel (Abstr., 1909, ii, 716, and preceding abstract) and by Hallwachs (Abstr., 1909, ii, 952). H. M. D.

Photo-galvanic Cells Formed with Uranous and Uranyl Sulphate. NICOLAY TITLESTAD (*Zeitsch. physikal. Chem.*, 1910, 72, 257—307. Compare Baur, Abstr., 1908, ii, 790).—The paper gives the results of a detailed investigation of the effect of light on the *E.M.F.* of cells containing uranous and uranyl sulphate, a phenomenon discovered and partly investigated by Baur (*loc. cit.*). Platinum electrodes were immersed in the same solution containing both uranous

and uranyl sulphate, and the potential difference measured when one electrode was illuminated and the other kept in the dark.

In the dark, the *E.M.F.* of urano-uranyl cells is represented by the equation: $E = e + RT/2F.\log_e[UO_2^{\cdot\cdot}][H^{\cdot}]^4/U^{\cdot\cdot\cdot\cdot}$, corresponding with the chemical change: $UO^{2\cdot\cdot} + 4H^{\cdot} \longrightarrow U^{\cdot\cdot\cdot\cdot} + 2H_2O + 2F$. e is 0·404 volt more positive than the normal hydrogen electrode.

Illumination displaces the potential towards the negative side, but this effect is observed only with smooth electrodes. The displacement of potential is approximately proportional to the logarithm of the light intensity.

The initial velocity of the displacement of equilibrium on illumination is proportional to the light intensity. The maximum potential cannot be obtained by simple superposition of the curves representing the displacement of the potential on illumination (displacement curve) and the return to the former potential on removing the source of light (return curve) respectively; under equivalent conditions the return is more rapid in the dark than in the light.

The velocity of displacement is practically independent of external circumstances, but the velocity of return increases with increasing concentration and temperature, and with diminution in the sulphuric acid concentration. From these results it follows that the law of mass action does not apply to such cells.

Small amounts of alcohol affect the light potentials slightly. On repeated illumination, the electrodes become slightly more positive. No satisfactory explanation of this observation has been found.

The absorption of the sulphate solutions has been measured with a Vierordt spectrophotometer. In the case of uranous sulphate, the absorption ratio : concentration/extinction-coefficient diminishes with dilution, indicating increased absorption. This is ascribed to change in the electrolytic dissociation of the salt.

The photochemical effect is greatest in the blue and violet for the wave-lengths 484—423. G. S.

Oxidation Potential of the Oxalates of Iron and of the Oxalate Ion. C. SCHAPER (*Zeitsch. physikal. Chem.*, 1910, **72**, 308—322).—The potential of cells containing solutions of potassium ferrous oxalate, $K_2Fe(C_2O_4)_2$, and potassium ferric oxalate, $K_3Fe(C_2O_4)_3$, have been measured in the dark at 17°, and in a few cases at 25° and 30°, and are shown to be satisfactorily represented by the formula: $E = \epsilon + 0{\cdot}058 \log_e[Fe(C_2O_4)_3''']/[Fe(C_2O_4)_2''] \times [C_2O_4'']$. The required data on the right in this equation are chiefly obtained from Schäfer's measurements (compare Abstr., 1905, ii, 499). The electrolytic dissociation constant, $[Fe^{\cdot\cdot}][C_2O_4'']/FeC_2O_4$, is $4{\cdot}36 \times 10^{-3}$ at 25°; the constant, $k = [Fe(C_2O_4)_2'']/[FeC_2O_4] \times [C_2O_4'']$, is $0{\cdot}7 \times 10^3$.

The complete solubility diagram for the system formed by potassium, ferrous, and ferric oxalates at 25° has been constructed, the available data being supplemented by some further measurements.

The oxidation of potassium ferrous oxalate to potassium ferric oxalate by carbon dioxide has been shown to occur by keeping a solution saturated with potassium oxalate and nearly saturated with ferrous oxalate in contact with carbon dioxide at 50 atmospheres

pressure for eight days, and then titrating the solution with potassium permanganate. Although the errors of measurement are large, it appears that about 10% of the ferric salt is oxidised under the experimental conditions. It is therefore probable that an equilibrium exists, represented by the equation: $Fe(C_2O_4)_2'' + \frac{1}{2}C_2O_4'' + CO_2 \rightleftarrows Fe(C_2O_4)_3'''$, and the equilibrium constant, $k = 1/(450[C_2O_4'']^{\frac{1}{2}})$, at room temperature. From this result it is calculated that the potential of the oxalic acid–carbon dioxide electrode, $E_{CO_2/C_2O_4''}$, is about $-0{\cdot}1$ volt for an oxalate concentration of 1 mol. per litre and a pressure of carbon dioxide equal to 1 atmosphere. G. S.

[Photochemistry.] EMIL BAUER (*Zeitsch. physikal. Chem.*, 1910, **72**, 323—337. Compare Abstr., 1908, ii, 790, and preceding abstracts). —The results described in the preceding papers are discussed, and in some cases explanations are suggested. The most important result is that the law of mass action does not hold for photochemical displacements of equilibrium. The general deductions as to photochemical equilibrium made by some previous observers (compare Wildermann, Abstr., 1902, ii, 545) are thus rendered untenable. G. S.

Nature of Electricity and its Connexion with Chemical Reactions. CAMILLE GILLET (*Bull. Soc. chim. Belg.*, 1910, **24**, 125—166).—The author supposes that the atoms of all the elements are built up of primary units, which are termed atomic particules in order to distinguish them from electrons. The kinetic energy of the vibrating particules is a measure of the electrical energy of a substance. In terms of these particules an interpretation of various physico-chemical facts is attempted. H. M. D.

Influence of the Metal of the Spark Gap on the Frequency of Electrical Vibrations. MAX WIEN (*Physikal. Zeitsch.*, 1910, **11**, 282—287).—It has been found that the resonance curves obtained for the discharge of a condenser vary in form according to the metal of which the electrodes are composed. This variation is not confined to the breadth of the curves, but a distinct shift in the position is observable. In the case of silver, this shift corresponds with an increase in frequency amounting to about 1% as compared with magnesium. H. M. D.

Slow Neutralisation of the Ions Produced in Certain Chemical Reactions. HENRI JACQUES PROUMEN (*Bull. Soc. chim. Belg.*, 1910, **24**, 167).—The products of combustion from a flame have been found to possess measurable conducting power after passing through a cooled tube 3 metres in length. The ionisation effects are greatly increased by diminishing the supply of oxygen to the burning gas. H. M. D.

Chemical Actions and Ionisation by Splashing. LÉON BLOCH (*Compt. rend.*, 1910, **150**, 694—696. Compare Abstr., 1908, ii, 1032; 1909, ii, 781; Broglie, Abstr., 1909, ii, 535, 637).—It has been suggested by Broglie and others that the electrical charge of

gases prepared in the wet way is due to the splashing of bubbles of gas in the liquid. Evidence is brought forward to show that this explanation is insufficient. When zinc is dissolved in hydrochloric acid, the initial sign of the charge carried by the gas depends on the state of the metal; when the gas bubbles are small, it is negative, whilst when the action is brisk and the bubbles are large, the charge is positive. The sign, moreover, varies during the reaction, changing from positive to negative as the action slackens. The amount of ionisation is independent of the amount of hydrogen evolved, but is influenced considerably by the addition of certain liquids to the mixture. Benzene, which does not become charged by agitation (splashing), inhibits ionisation; alcohol or acetone, on the other hand, have a transient inhibitory effect, which disappears when the liquid has become diffused through the acid. These two liquids become charged on agitation.

The author considers that ionisation by chemical action or by splashing is entirely a surface phenomenon. W. O. W.

Conduction of Electricity through Solid Silver Chloride. MAX LE BLANC and FRITZ KERSCHBAUM (*Zeitsch. Elektrochem.*, 1910, **16**, 242—244).—A cylinder of solid silver chloride was cast between two small platinum electrodes; when an *E.M.F.* of 10 volts was applied, a current of about 10^{-7} ampere passed through the salt, indicating a resistance of many million ohms. The current soon begins to increase, and, after five or six days, reaches a nearly constant value, corresponding with a resistance of about 40 ohms. The silver chloride was absolutely unchanged in appearance, and no polarisation could be observed. The conduction appeared to obey Ohm's law. The preparation of the silver chloride was modified in several ways (it was made in the dark); the cylinder was protected from radiation by casting a lead casing round it without changing the character of the phenomena. Interrupting the current makes very little difference in the resistance of the silver chloride, also heating to near its melting point has little influence.

If an alternating current is substituted for the direct current, however, the resistance very soon increases to the original large value, but, curiously enough, when the direct current is again used, the good conductivity is regained very quickly.

To make sure that no change had occurred in the silver chloride, 4 grams of it, through which 6 ampere hours had passed, were cut up into an anode, a cathode, and a middle layer, and each of them analysed. They were pure silver chloride. T. E.

Conductivity of the Halogens in Nitrobenzene. LUDWIK BRUNER [with A. GALECKI] (*Zeitsch. Elektrochem.*, 1910, **16**, 204—205). —Solutions of bromine and iodine in incompletely dry nitrobenzene conduct electricity well, solutions of chlorine do not.

Solutions in perfectly dry nitrobenzene are non-conductors.

When the conducting solutions are electrolysed, bromine or iodine is separated at the anode in theoretical quantity. Reduction takes

place at the cathode. Migration measurements show that the current is carried by a halogen complex, which migrates towards the anode.

T. E.

Formation of Salts from the Physico-chemical Standpoint. IV. GIUSEPPE BRUNI and C. SANDONNINI (*Zeitsch. Elektrochem.*, 1910, **16**, 223—227. Compare Abstr., 1908, ii, 935, 1012; 1909, ii, 115).—In a previous paper it was shown that when an acid which follows Ostwald's dilution law is neutralised by the successive addition of small quantities of a base, the conductivity of the solution passes through a minimum when the fraction of the acid neutralised, $x_{,} = KV + 2A\sqrt{KV}/\sqrt{1-A^2}$, where $A = 1 - 2(l_M + l_A)/(l_H + l_A)$. A similar expression should hold when a weak base is neutralised by a strong acid. This is tested for the neutralisation of ammonia and mono-, di-, and tri-methylamines by hydrochloric acid. When A is negative there may be no real minimum for small values of V (stronger solutions). The experimental results are in very good agreement with the theory. With the three methylamines, the strongest solution ($V=16$) showed no minimum, but it appeared at greater dilutions, and the calculated values of x agree very closely with those observed. Ammonia shows no minimum even at the greatest dilution ($V=1024$), and the theory indicates that it should appear first at $V=2087$.

T. E.

Formtion of Salts from the Physico-chemical Standpoint. V. C. SANDONNINI (*Zeitsch. Elektrochem.*, 1910, **16**, 227—229).—The conductivity of solutions containing acetic acid and barium, calcium, zinc, and cobalt acetates is measured. The acetate strength of the solutions is kept constant, and the proportion combined with the base varied between 0 and 100%. The results are very similar to those described in the preceding abstract (Bruni and Sandonnini), a minimum conductivity being observed at greater dilutions. The value of x (the fraction of the acid present in the salt form) for the solutions of minimum conductivity is calculated from the expression given (preceding abstract), and a very good agreement with the observations is found.

T. E.

Influence of Dissolved Gases on the Electrode-potential in the System Silver–Silver Acetate. ARTHUR JAQUES (*Trans. Faraday Soc.*, 1910, **5**, 212—224).—A large number of measurements of the *E.M.F.* of the cell Ag | $AgC_2H_3O_2$ saturated sol. | NH_4NO_3 saturated sol. | $0{\cdot}1N$-calomel electrode at 25° are recorded. When ordinary distilled water is used in making the silver acetate solution, variable results are obtained, but constant *E.M.F.*'s are obtained by blowing hydrogen, carbon dioxide, oxygen, or nitrogen through the solution which are different for each gas. With hydrogen the *E.M.F.* is 0·3816 volt, which agrees with the value calculated from the *E.M.F.* of a cell containing silver nitrate instead of acetate. Oxygen and nitrogen give about the same value (0·35 to 0·36). Weak solutions are still more sensitive to gases, and in $0{\cdot}01N$-silver acetate solution

saturated with hydrogen the *E.M.F.* increases rapidly with the temperature.

The corresponding cells containing silver nitrate or lead acetate or nitrate exhibit no measurable variations with different gases.

T. E.

Electrochemical Investigation of Fluid Amalgams of Thallium, Indium, and Tin. I. THEODORE W. RICHARDS and J. HUNT WILSON (*Zeitsch. physikal. Chem.*, 1910, 72, 129—164. Compare Richards and Forbes, Abstr., 1907, ii, 424).—The potentials between amalgams of thallium, indium, and tin have been measured at 0° and 30°. The results with the thallium cells are regarded as accurate to within 0·00001 volt, those with indium and tin to 0·000005 volt.

The potentials for thallium and indium amalgams are higher (in the case of indium only slightly higher), and those for tin amalgams lower, than those calculated according to the gas laws, but in all cases the deviations between observed and calculated values tend to disappear as the amalgams become more dilute. The temperature-coefficient of the *E.M.F.* between 0° and 30° is for thallium and indium amalgams slightly lower, and for tin amalgams slightly greater, than the value calculated according to the gas laws, 0·00366, but in this case, also, the coefficient approximates to the ideal value with increasing dilution.

Cady's equation (Abstr., 1899, ii, 394) gives in all cases a fairly accurate representation of the deviations from the simple gas laws. The heats of dilution have been calculated by means of the Helmholtz formula in the usual way, and they agree as regards sign and order with the experimental values. Attempts to determine the heat of dilution of thallium and indium amalgams directly did not lead to very satisfactory results.

Experiments with quadrivalent tin as stannic chloride and sodium stannate did not lead to conclusive results. The experimental results of Cady on this subject (*loc. cit.*), are regarded as untrustworthy.

The density of pure iridium is 7·28 at 20°. The densities of a number of dilute fluid amalgams of thallium, indium, and tin have been determined by a pyknometer method. G. S.

Electrochemical Investigation of Fluid Amalgams of Zinc, Cadmium, Lead, Copper, and Lithium. II. THEODORE W. RICHARDS and R. N. GARROD-THOMAS (*Zeitsch. physikal. Chem.*, 1910, 72, 165—201. Compare preceding abstract).—The measurements of Richards and Forbes (*loc. cit.*) with zinc amalgams have been repeated and extended, and the temperature-coefficients of the cells have also been determined. Similar measurements have also been made with lead amalgams. The potential values for lead, like those for tin and zinc, are less than those calculated according to the gas laws, but the deviations tend to disappear with increasing dilution.

Copper and iron are not sufficiently soluble in mercury to admit of satisfactory quantitative measurements, and on this account the results of previous observers are of no value. The solubility of copper in

mercury is 0·0024%, that of iron, 0·00134%, by weight. As lithium is only soluble to the extent of 0·0036% by weight in mercury, only a few measurements were made with this amalgam, and these are not quite accurate on account of the difficulty of finding a suitable electrolyte.

The majority of the deviations from the simple gas laws are connected with the heat of dilution of the amalgams, and are therefore represented satisfactorily by Cady's formula (*loc. cit.*). Those which cannot be accounted for in this way are ascribed to polymerisation of the solute, or to combination of solvent and solute according as the observed values are higher or lower than the calculated values.

A deduction from Cady's equation, that the temperature-coefficient of a cell made up with amalgams is equal to the ideal potential of the cell (calculated from the relative concentration of the amalgams) divided by the absolute temperature, and is independent of the temperature, is approximately confirmed by the experimental results. Hence the temperature-coefficient of the *E.M.F.* of such a cell can be approximately calculated without making *E.M.F.* measurements.

The heats of dilution can be calculated more accurately by means of the Helmholtz formula than by means of Cady's formula. G. S.

Decomposition Potentials. KURT BENNEWITZ (*Zeitsch. physikal. Chem.*, 1910, **72**, 202—224).—The uncertainty attaching to the determination of decomposition potentials from the experimental observation of "breaks" on the curves representing the variation of the strength of current with change of *E.M.F.* is, to some extent, removed by the use of rotating electrodes, a method of procedure which has already been used by some previous observers. In these circumstances it has been found possible to derive a formula which admits of the deduction of the position of breaks from the experimental data. The method sometimes used of plotting the logarithm of the current against the *E.M.F.* leads to inaccurate results in the neighbourhood of the breaks.

The formula in question leads to the conclusion that in the electrolysis of dilute sulphuric acid with platinum electrodes, a point of decomposition occurs between 1·50 and 1·63 volts (referred to the hydrogen electrode as zero), and that the position of this break will be lower with platinised than with smooth electrodes. The actual position of the break with platinised electrodes is 1·46 volts, and it is suggested that the decomposition only occurs at this potential at certain points on the electrode, and becomes general at the higher potential deduced from the formula.

The breaks found by previous authors, at 1·47 and 1·95 volts, in the electrolysis of sulphuric acid have not been observed by the present method, but there is a definite break at 2·20 volts when concentrated sulphuric acid, containing alkali hydrogen sulphate, is electrolysed; this corresponds in all probability with the formation of persulphuric acid according to the equation: $2HSO_4' = H_2S_2O_8 + 2F$.

The generally accepted break at 1·08 volts has only been observed on the non-stationary curve, and is probably connected with the passivity of platinum, but a definite break at 0·76 volt has been observed on the curves for stationary and non-stationary conditions.

The latter point is probably connected with the formation of oxides or hydroxides of platinum, but the metal is not passive under these conditions. G. S.

Potential Difference between Two Electrolytic Solutions. H. PLEYEL (*Zeitsch. physikal. Chem.*, 1910, **72**, 1—37).—Planck, Guyot (compare Abstr., 1908, ii, 656), and others have derived equations for the difference of potential between two solutions of electrolytes, with certain restrictions as to the nature of the solutions, and the author now gives a general solution of the problem, applicable to any solutions. In the second part of the paper the formulæ are applied to determine the potential differences between the following pairs of solutions. I, Barium chloride, II, hydrochloric acid; I, barium chloride 0·04 mol. per litre, zinc chloride 0·05 mol. per litre, II, potassium chloride 0·03 mol. per litre, sodium chloride 0·01 mol. per litre; I, copper sulphate, II, hydrochloric acid. These solutions are chosen as being typical of the different kinds of valency which may be met with in such investigations. G. S.

Electromotive Force of the Hydrocyanic Acid Cell. R. NAUMANN (*Zeitsch. Elektrochem.*, 1910, **16**, 191—199).—The cells were built up with platinum electrodes dipping into solutions of potassium cyanide, either pure or mixed with sulphuric acid. Cyanogen was passed through one solution, hydrogen through the other. The partial pressure of hydrogen cyanide vapour in equilibrium with the solutions was measured by passing hydrogen through them and weighing the hydrogen cyanide carried away, in the form of silver cyanide. The *E.M.F.* of the cells increased fairly quickly to a maximum and then fell slowly, owing to changes produced by the hydrolysis of the cyanogen in the alkaline solutions. The final results are

Solution.	Temperature.	*E.M.F.* in volts.	Pressure of HCN in mm.
0·1*N*-KCN	25°	0·984	0·1324
0·01*N*-KCN	0	1·042	0·0427
	25	1·111	—
	50	1·171	—
0·002*N*-KCN	25	1·125	0·0191
0·001*N*-KCN	25	1·160	0·01351
500 c.c. 0·1*N*-KCN + 50 c.c. 1·032*N*-H_2SO_4	25	0·835	7·01
400 c.c. 0·1*N*-KCN + 5 c.c. 1·032*N*-H_2SO_4	25	0·904	0·568

The vapour pressures of the potassium cyanide solutions are calculated from a measurement with a normal solution which gave 0·3618 mm.

From the measurements with 0·01*N*-solutions, the heat of formation of hydrogen cyanide from hydrogen and cyanogen is calculated to be 6650 cals., instead of 5570 cals. found calorimetrically, which indicates that the change determining the *E.M.F.* of the cell is really the formation of hydrocyanic acid.

The equilibrium constant of the reaction, $K = p_{H_2} \cdot p_{C_2N_2} / p^2_{HCN}$, is then calculated from the measurements; the average value of $\log_{10} K$

is $-10 \cdot 14$ at 25°. Introducing this value into Nernst's approximate formula, the value $-2 \cdot 24$ is found for $\Sigma \nu C$ (the sum of the products of the numbers of molecules and the corresponding chemical constants). This indicates that hydrogen cyanide possesses a relatively large chemical constant. T. E.

Thermo-electric Properties of Metallic Alloys. WERNER HAKEN (*Ber. Deut. physikal. Ges.*, 1910, 229—239 *).—Measurements have been made of the thermo-electric forces which are developed at the junctions of copper and alloys formed from the following pairs of elements: tellurium–antimony, tellurium–tin, tellurium–bismuth, tellurium-lead, antimony–silver, copper–phosphorus. The curves which represent the dependence of the thermo-electric force on the composition of the alloy are compared with the corresponding binary freezing-point curves, and also with the curves showing the variation of the electrical conductivity with the composition of the alloy. This comparison shows that the measurement of the thermo-electric force can be used as a sensitive test for the formation of definite compounds, and also for detecting the formation of mixed crystals. Such measurements are recommended as a means of testing the conclusions drawn from the investigation of the phenomena of solidification.

H. M. D.

Ionisation in Aqueous Solutions of Lead and Cadmium Acetates. ARTHUR JAQUES (*Trans. Faraday Soc.*, 1910, **5**, 225—243).—The concentrations of the lead or cadmium ions in the solutions is measured by means of the *E.M.F.*'s of concentration cells with and without the addition of sodium and potassium acetates. The total numbers of ions and molecules are obtained from the freezing points, and the concentrations of the acetate ion from measurements of the solubility of silver acetate in the solutions. Applying the law of the action of mass to the data so obtained, the author draws the conclusions that there are comparatively few complex ions in solutions of lead or cadmium acetate, and that the complex ions are $PbAc_3'$ and $CdAc_3'$ respectively. The quantity of complex ion and its complexity increases, however, very rapidly when sodium or potassium acetate is added to the solution in increasing quantity. The dissociation of the single acetates takes place in two steps: $M(C_2H_3O_2)^2 \rightleftharpoons M(C_2H_3O_2)^{\cdot} + (C_2H_3O_2)'$ and $M(C_2H_3O_2)^{\cdot} \rightleftharpoons M^{\cdot\cdot} + (C_2H_3O_2)'$. For lead acetate the dissociation constants of the two stages are $>0 \cdot 04$ and $0 \cdot 0021$ respectively, whilst the dissociation constant of the complex ion is not greater than 10^{-5}. For cadmium acetate the two dissociation constants are about $0 \cdot 2$ and $0 \cdot 01 \pm 0 \cdot 002$ respectively, that of the complex ion being not greater than 5×10^{-4}. The normal potential of cadmium is $-0 \cdot 732 \pm 0 \cdot 006$ volt compared with the $N/10$-calomel electrode at 25°. T. E.

Electrolytic Reduction of Acetophenone and Benzophenone. ERICH MÜLLER [with KOPPE] (*Zeitsch. Elektrochem.*, 1910, **16**, 236—240).—Kaufler (Abstr., 1907, ii, 924) has stated that acetophenone and benzo-

* and *Ann. Physik*, 1910, [iv], **32**, 291—336.

phenone are reduced electrolytically at a platinum cathode which is kept hot by an independent electric current, whilst they are not reduced if the heating current is not used.

The author has repeated these experiments, and finds that the heating current has no appreciable effect on the reduction in the case of benzophenone, which is reduced with a current efficiency of some 60%, at a smooth platinum cathode whether it is heated or not.

With acetophenone the heating diminished the current efficiency somewhat.

With platinised electrodes no reduction was observed in either case, whether the electrode was heated or not. T. E.

Magnetic Properties of Manganese, Vanadium, and Chromium. PIERRE WEISS and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, **150**, 687—689).—The magnetic properties of manganese, vanadium, and chromium are not intensified by cooling these elements in solid hydrogen. At this low temperature, however, ferrous sulphate becomes much more magnetic. According to Curie's law, the magnetism of the foregoing metals should increase considerably on cooling; it is probable, therefore, that these elements exhibit paramagnetism of a new type.

Pure manganese, prepared by decomposition of the amalgam by heat, is paramagnetic; on heating, however, it becomes ferromagnetic.

W. O. W.

Relationship of Some Thermal Quantities. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1910, **16**, 132—135).—Assuming that the specific heats of two condensed modifications of a substance are equal at absolute zero, and that they are linear functions of the temperature, their difference may be written $c_2 - c_1 = aT$. Nernst's theorem then leads to the equations:

$$A = U_o - \tfrac{1}{2}aT^2$$
$$U = U_o + \tfrac{1}{2}aT^2,$$

where A and U are the changes of free and internal energy accompanying the transformation of one modification into the other. At the transition temperature, T_u, $A = 0$; therefore $U_u = (c_{u_2} - c_{u_1})T_u$.

The molecular depression of the freezing point or transition point of a substance, $R.T_u^2/Q_u = k$, is a quantity which is easily determined experimentally, and since for condensed systems Q_u and U_u are practically identical, we obtain $R/k = a$, or $c_{u_2} - c_{u_1} = RT_u/k$.

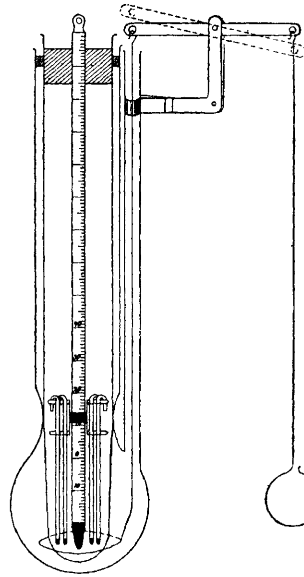
For acetic acid, for example, the difference of the specific heats of liquid and solid acid calculated by means of the last formula is 0·147, whilst direct determinations give 0·145. A similarly good agreement is found for the rhombic and monoclinic modifications of sulphur.

T. E.

Apparatus for Melting-point Determinations. K. MATTON (*Zeitsch. angew. Chem.*, 1910, **23**, 557).—The apparatus is constructed with the idea of preventing an escape of injurious sulphuric acid fumes, and also to get more accurate thermometric readings.

The narrow part of the apparatus is closed with a tube drawn out

conically, which causes the fumes to enter the lateral tube, in which they are quickly condensed; the space for reading the degrees always remains unclouded. The stirrer passing down the lateral tube allows the continuous mixing of the sulphuric acid and the even distribution of temperature.



A decided advantage of the instrument is that several melting points may be determined simultaneously when the tubes, after introducing the substance, are bent and suspended from the holder attached to the thermometer, as shown in the figure. L. DE K.

Raising and Lowering of the Freezing Point. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1910, 7, 333—335).—An application of the author's graphic method, showing that addition of another substance first raises the freezing point of a binary solution to a maximum, and then causes it to fall again. An aqueous solution of triethylamine exhibits this phenomenon on addition of phenol, the freezing point rising in one experiment from $-11{\cdot}7°$ to $-5{\cdot}3°$, and in another experiment from $-8{\cdot}8°$ to $-7{\cdot}9°$, then to $-6°$, and finally to $-4{\cdot}6°$. A. J. W.

Depression of Freezing Point in very Dilute Aqueous Solutions. T. G. BEDFORD (*Proc. Roy. Soc.*, 1910, *A*, 83, 454—461). —The freezing points of dilute solutions of various electrolytes have been compared with that of water by a method similar to that previously described by Griffiths. From the observed depression, the degree of ionisation (a) is deduced and this is compared with the corresponding value (a') obtained from Whetham's measurements of the electrical conductivity at 0°. The values of a and a' for solutions of potassium chloride, permanganate, and ferricyanide, magnesium sulphate, copper sulphate, barium chloride, and sulphuric acid containing n gram-molecules per 1000 grams of solution are tabulated in the original.

Except in the case of potassium ferricyanide, the values of a are less than those of a', and the divergence between the two series of numbers increases with increasing concentration. The abnormal behaviour of potassium ferricyanide is difficult to account for, seeing that the molecular depression in very dilute solution corresponds almost exactly with that required by complete ionisation with the production of four ions.

Measurements were also made for solutions of potassium dichromate. At all the concentrations examined, the molecular depression is greater than $5{\cdot}58$, which would correspond with complete ionisation into three ions. It is supposed that the salt reacts with water in such a way as to produce a larger number of ions. H. M. D.

Reciprocal Cryoscopic Behaviour of Substances containing the Groups $-CO-$ and $-CH_2-$ Respectively. LUIGI MASCARELLI and I. MUSATTY (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 213—218. Compare Abstr., 1909, ii, 972).—The authors have studied the cryoscopic behaviour of the two pairs of compounds: (1) diphenylmethane and benzophenone, and (2) dibenzyl and benzil, each member of the pairs being used as both solvent and solute.

Bruni and Amadori (private communication) find the mean value 67·2 for the cryoscopic constant of diphenylmethane. Eykman (Abstr., 1890, 324) found 66·4, and Padoa, 71. For benzophenone, the measurements of Padoa and Galeati (*Gazzetta*, 1905, **35**, i, 189) give the value 98·0, which agrees with that found by Eykman (*loc. cit.*). The behaviour of naphthalene in freezing dibenzyl confirms Garelli and Calzolari's value, 72 (Abstr., 1899, ii, 732), for the cryoscopic constant of this solvent; using this number in van't Hoff's formula, the value 29·3 is obtained for the latent heat of fusion, whilst Bogojawlensky and Winogradoff's direct measurements (Abstr., 1908, ii, 806) gave 30·36.

For benzil, Auwers (Abstr., 1900, ii, 66) found the cryoscopic constant 105, which gives 20·4 for the latent heat of fusion, Bogojawlensky's measurements (Abstr., 1905, ii, 799) giving 22·25. The authors find that the freezing point of benzil gradually rises when it is fused, so that it must be kept fused for a considerable time (four to five days) before being used for cryoscopic determinations.

Eykman (*loc. cit.*) found that diphenylmethane exhibits normal cryoscopic behaviour in benzophenone, and the same is now found to be the case with benzophenone in diphenylmethane. Similar results are obtained with the two compounds benzil and dibenzyl.

T. H. P.

A Special Case of Evaporation. PIERRE VAILLANT (*Compt. rend.*, 1910, **150**, 689—691).—The author has determined at different temperatures the rate of evaporation in the case of a number of liquids at rest in a long, cylindrical brass tube. The results, which are given in tabular form, are in good agreement with the equation $\sigma q/\sigma t = b(MF)(t/300)^{-n}$, when q is the weight of liquid evaporated in the time t, M the molecular weight of the vapour, and F the maximum vapour pressure in the tube; b and n vary slightly according to the liquid under examination. In each case n is less than 0·5, and appears to have a greater value in easily volatile liquids than in those which evaporate more slowly.

W. O. W.

Influence of Pressure on the Boiling Points of Metals. HAROLD C. GREENWOOD (*Proc. Roy. Soc.*, 1910, *A*, **83**, 483—491).—The influence of pressure on the boiling points of bismuth, copper, lead, silver, tin, and zinc has been determined. Two types of apparatus suitable for measurements respectively below and above atmospheric pressure are described. In an atmosphere of nitrogen, bismuth boils at 1200° and 1310° under 102 and 257 mm. pressure; copper at 1980° and 2180° under 100 and 257 mm.; lead at 1320° and 1420° under 105 and 266 mm.; silver at 1660° and 1780° under 103 and 263 mm.; tin at 1970° and 2100° under 101 and 262 mm. respectively. For

pressures greater than atmospheric, bismuth was found to boil at 1420°, 1740°, 1950°, and 2060° under 1, 6·3, 11·7, and 16·5 atmospheres; lead at 1525°, 1870°, and 2100° under 1, 6·3, and 11·7 atmospheres; zinc at 1120°, 1230°, 1280°, and 1510° under 6·3, 11·7, 21·5, and 53 atmospheres respectively. The results show that the influence of pressure on the boiling points of the metals is very considerable. H. M. D.

Adiabatic Determination of the Heats of Solution of Metals in Acids. I. THEODORE W. RICHARDS and LAURIE LORNE BURGESS (*J. Amer. Chem. Soc.*, 1910, **32**, 431—460).—A discussion is given of Thomsen's work on the heats of solution of metals in acids, and the chief sources of inaccuracy in his results are pointed out.

In the present paper an account is given of the application of the method of adiabatic calorimetry (Abstr., 1905, ii, 677; 1907, ii, 604; 1908, ii, 806) to the determination of these constants. The apparatus and method are described in detail, and means of avoiding the introduction of errors are pointed out. Since the solution of metals in acids takes a considerable time, the adiabatic method is well adapted to the determination of the energy change involved. In order to equalise the temperature during the reaction, the liquid must be thoroughly stirred. Determinations have been made of the heat developed by stirring, in order that the necessary corrections can be applied; it has been found that the quantity of heat thus generated is increased nearly ten times by doubling the rate of stirring. The loss of heat produced by the evaporation of the solution into the escaping hydrogen has been determined, and the necessary correction applied. An account is given of the means employed to ensure the purity of all the materials used in the investigation. The quantity of oxide on the surface of the metals was found to be exceedingly small. It is shown that the method adopted by Thomsen of calculating the heat of solution of a metal in dilute acid from the data obtained with concentrated acid leads to inaccurate results.

The heats of solution of zinc, aluminium, magnesium, cadmium, and iron in an excess of hydrochloric acid at 20° have been determined; the results are tabulated. E. G.

Adiabatic Calorimeter for Use with the Calorimetric Bomb. FRANCIS G. BENEDICT and HAROLD L. HIGGINS (*J. Amer. Chem. Soc.*, 1910, **32**, 461—467).—In connexion with the determination of the potential energy of food, fæces, and urine by means of the calorimetric bomb, a suitable adiabatic calorimeter has been devised, in which the temperature of the outer water jacket is controlled by electric heating. The apparatus is described with the aid of a diagram. A constant temperature of the calorimeter system can be readily obtained both at the beginning and end of a combustion. The calorimeter has proved very efficient, and enables combustions to be carried out much more quickly than was formerly the case. E. G.

Simple System of Thermodynamic Chemistry, Based on a Modification of the Method of Carnot. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1910, **32**, 467—502).—A modification of Carnot's

method is described, in which the cycle of operations is reduced to a single step, and enables the desired relation to be written down by inspection. It also ensures that the differential equation so obtained will always be entirely rigorous, since it is impossible to introduce into the process any assumption except the second law of thermodynamics. This has been achieved by joining together the pistons of the ordinary cycle so as to form a single complete engine, which is termed the "perfect thermodynamic engine." This simplified process is illustrated by using it to derive certain fundamental relations.

In applying the engine to the subject of chemical equilibrium, the following facts have been brought to light. The conclusion drawn by Robertson (Abstr., 1906, ii, 833), that the law of mass action is an expression of the condition for equilibrium in a system in which the equation $p(V-d)=RT$ is obeyed, is shown to be erroneous. The statement of Stieglitz (Abstr., 1908, ii, 673), that the theoretical basis for the solubility product law in the case of strong electrolytes is destroyed by the fact that they do not obey the law of mass action, is not justified.

It is shown that many equations containing the van't Hoff i involve an unnecesssary number of assumptions, and that each equation can be split up into two simpler equations, one involving only the ions, and the other the non-ionised molecules. The advantage of this process is illustrated by reference to the data obtained by Noyes and Sammet on the solubility of *o*-nitrobenzoic acid (Abstr., 1903, ii, 468).

E. G.

Heat of Hydration of Sodium Sulphate. J. P. WUITE (*Chem. Weekblad*, 1910, 7, 250—251. Compare Jorissen, this vol., ii, 269, and next abstract).—Polemical. A reply to Jorissen's criticism.

A. J. W.

Heat of Hydration of Sodium Sulphate. WILLEM P. JORISSEN (*Chem Weekblad*, 1910, 7, 251—253). Polemical. A reply to Wuite (preceding abstract).

A. J. W.

Calorimetrical Analysis of Hydrated Salts. FREDERICK G. DONNAN and GEOFFREY D. HOPE (*Trans. Faraday Soc.*, 1910, 5, 244—250). —When successive quantities of water are removed slowly from a hydrated salt, a mixture of the original hydrate and the next lower one will probably be formed. It is shown that the heat of solution of such a mixture is a linear function of the quantity of water present, each pair of hydrates giving one straight line. By plotting the heats of solution against the molecules of water per molecule of anhydrous salt in the mixtures, a series of straight lines is obtained, which intersect at points corresponding with the composition of the different hydrates. The method is applied to sodium carbonate and copper sulphate, the hydrates indicated being Na_2CO_3,H_2O; $Na_2CO_3,7H_2O$; $Na_2CO_3,10H_2O$; $CuSO_4,H_2O$; $CuSO_4,5H_2O$. There is no indication of the existence of the trihydrate of copper sulphate; this may be due to insufficient accuracy of the experiments.

T. E.

Simple Relationships between the Density and the Index of Refraction of a Solution and its Volume Concentration. G. FOUQUET (*Bull. Assoc. Chim. Sucr. Dist.*, 1910, **27**, 848—855).—By reference to data for the densities of sucrose solutions, the author considers the accuracy with which the density can be represented by a formula of the type $d_4^t - 1 = Ka$, in which a is the quantity of sucrose in 100 c.c. of solution at temperature $t°$, and K is a constant. The smaller the range of the concentration the better is the agreement between experiment and the values given by the equation. As the range of concentration increases, different values must be given to K to obtain the best results.

The refractive indices at 20° of sucrose solutions of widely varying concentration can be represented fairly satisfactorily by the equation $n = 1{\cdot}3330 + 0{\cdot}0014\ a$. H. M. D.

New Method for Determining Vapour Densities. PHILIP BLACKMAN (*Chem. News*, 1910, **101**, 121—123).—A summary of work already published (compare Abstr., 1908, ii, 561; 1909, ii, 21, 643.

G. S.

Expansion of Benzene, Chlorobenzene, Bromobenzene, and their Solutions. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 135—166).—The author has made accurate measurements of the densities at 0° or 20°, and of the expansion between 0° and 80° of benzene, chlorobenzene, bromobenzene, and their binary mixtures. Mendeléeff's simple formula, $V_t = V_0/(1 - kt)$, does not express the author's results, since the coefficient of expansion changes with the temperature in all cases; so that the coefficient k is replaced by $k_1 + k_2t^2$, giving $V_t = V_0/(1 - k_1t - k_2t^3)$.

For benzene, $k = 0{\cdot}00118082 + 0{\cdot}000000003649\ t^2$, which does not agree with the results of Walden (Abstr., 1909, ii, 122), who found that, for benzene and a number of other liquids, the coefficient of expansion is a constant magnitude. The numerical results obtained are compared with those of Kopp (*Ann. Phys. Chem.*, 1847, **72**, 239), Luginin (*Ann. Chim. Phys.*, 1867, [iv], **11**, 453), and Walden (*loc. cit.*).

For chlorobenzene, D_4^0 1·12792, D_4^{30} 1·10643, $k = 0{\cdot}00095342 + 0{\cdot}000000002114\ t^2$. The densities at various temperatures from 0° to 100° are in good agreement with those given by Perkin (Trans., 1896, **69**, 1202) and Young and Fortey (Trans., 1902, **81**, 768).

For bromobenzene, D_4^0 1·52231, D_4^{20} 1·49533, $k = 0{\cdot}00088764 + 0{\cdot}0000000009265\ t^2$. The results of the dilatometric measurements differ considerably from those obtained by Weger (Abstr., 1884, 8).

For bromo- and chloro-benzene, the magnitude of aT_k = const., where a represents the coefficients of expansion at corresponding temperatures, and T_k is the absolute critical temperature. The author's results are not in agreement with Walden's law (1), which states that the coefficient of expansion is inversely proportional to the critical temperature expressed in degrees centigrade: $kt_k = 0{\cdot}34$ for non-associated liquids; but they agree rather better with this author's second law, according to which the coefficient of expansion on the absolute scale, $K_0 = (v_2 - v_1)/(v_2T_2 - v_1T_1)$, is inversely proportional to the absolute critical temperature: $K_0T_k = 0{\cdot}488$ (*loc. cit.*).

The variation of the contraction constant K of the equation $D = Km_1m_2$ (compare Abstr., 1909, ii, 797) with the temperature is expressed by one of two types of curve: (1) with the mixture $C_6H_5Cl + C_6H_5Br$, K has a small negative value at low temperatures, the curve approaching the axis of zero contraction apparently asymptotically; (2) for $C_6H_6 + C_6H_5Br$ or $C_6H_6 + C_6H_5Cl$, the expansion occurring at low temperatures diminishes rapidly with rise of temperature, and changes into a quickly increasing contraction. The conditions of isofluidism (*loc. cit.*) are closely approached by mixtures of chloro- and bromo-benzene, whilst the solution $C_6H_6 + C_6H_5Br$ differs from an isofluid solution more than the solution $C_6H_6 + C_6H_5Cl$ does. One of the conditions of the isofluidism of two liquids is the equality of their critical pressures. T. H. P.

Variation with Temperature of the Contraction Occurring on Formation of Solutions of Normal Liquids. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.* 1910, **42**, 167—188).—In order to verify the relations between isofluidism, critical pressures, and agreement of the components of the solution with the law of corresponding states indicated in the preceding paper, the author has investigated the contraction at 0°, 20°, and 40° of pairs of liquids chosen from the following: esters, aromatic and aliphatic hydrocarbons, carbon tetrachloride, and chloro- and bromo-benzene, for the majority of which the critical temperatures are known sufficiently accurately.

The results show that the law of contraction on formation of solutions of normal liquids, expressed by the formula: $D = Km_1m_2$, or $d = kx(1-x)$, where d is the contraction per 1 mol. of solution, and x is the molecular proportion of one of the constituent liquids, holds unchanged for different temperatures, the contraction constant alone varying. For the maintenance of the first condition of isofluidism, namely, the absence of contraction ($K = k = o$), it is necessary that the two components belong to one and the same group of compounds obeying the law of corresponding states, and that their critical pressures are very nearly, possibly quite, equal. In one and the same group of compounds, the contraction constant is small if the difference of the critical pressures of the components is small, and vice versâ, but no direct proportionality exists. For compounds of different groups, the contraction constant may be very great for a small difference between the critical pressures. Two isofluid compounds may give with a third compound not isofluid with them, solutions with contractions of different magnitudes.

T. H. P.

Contraction Constant. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 188—194. Compare preceding abstracts).—Two liquids which go to make up a mixture undergo changes in volume dependent on alterations of their original internal pressures from P_1 and P_2 to some different value, P_x. These changes in volume would be $\beta_1(P_x - P_1)$ and $\beta_2(P_x - P_2)$ per unit-volume of the two components, where β_1 and β_2 are the coefficients of contraction. Hence, if there is no other factor influencing the volumes of the components on mixing, the volume v of 1 gram-mol. will be given by: $v =$

$[v_1 - \beta_1 v_1(P - P_1)]x + [v_2 - \beta_2 v_2(P - P_2)](1 - x)$, where x represents the concentration of one constituent. Further, $d = v_1 x + v_2(1 - x) - v$, and from this the above equation gives: $d = \beta_1 v_1(P - P_1)x + \beta_2 v_2(P - P_2)(1 - x)$ (I). In this expression P is an unknown function of x; assuming the function to be linear of the form $P = P_1 x + P_2(1 - x)$, equation (I) becomes: $d = (\beta_1 v_1 - \beta_2 v_2)(P_2 - P_1)x(1 - x)$, which is of the form $d = kx(1 - x)$, where $k = (\beta_1 v_1 - \beta_2 v_2)(P_2 - P_1)$; on this assumption, k is independent of x. If, however, the relation of P to x is represented by a simple parabolic function of the second degree, k will be a linear function of x.

These considerations are found to give a satisfactory explanation of the results described in the preceding abstracts, and to lead to the further conclusion that solutions of normal liquids possess additive internal pressures, whilst the other properties of these solutions would be more or less complex functions of the composition, but still dependent on this law and on the magnitudes of the internal pressures of the components (compare Tammann, Ueber die Beziehung zwischen den inneren Kräften und Eigenschaften der Lösungen, 1907).

T. H. P.

Viscosity and Fluidity. EUGENE C. BINGHAM (*Amer. Chem. J.*, 1910, **43**, 287—309).—In an earlier paper (Abstr., 1908, ii, 1017) it has been shown that fluidity data can be accurately represented by the formula $t = A\phi - B/\phi + C$.

It is now pointed out that there is a relationship between volume and fluidity, and that if fluidity is substituted for volume in Van der Waals' equation, the resulting expression reproduces fluidity data with considerable accuracy. In order to test the relationship further, a study has been made of Thorpe and Rodger's viscosity data in the neighbourhood of 4°, and it is shown that in the case of water there is a decrease of fluidity at these temperatures of corresponding magnitude with the decrease of volume.

Since the fluidity of liquids increases with the temperature, and that of gases decreases with the temperature, there must be a maximum in fluidity; the author proposes to ascertain whether this maximum is connected with the critical temperature.

It has been found that the fluidities of all aliphatic hydrocarbons and all ethers are nearly identical at the b. p., and data are now quoted which show that this relation between fluidity and vapour pressure is general for the hydrocarbons. Measurements of the vapour pressures of methyl propyl ether, ethyl propyl ether, and dipropyl ether at various temperatures between 0° and the b. p. have shown that the relation is also general in the case of the ethers, and it has also been found that at high temperatures the fluidity is a linear function of the vapour pressure.

The constants for different atoms and groupings at the fluidity 200 were given in an earlier paper (Bingham and Harrison, Abstr., 1909, ii, 382); the corresponding data for the fluidity 300 are now recorded, and the association of a number of substances has been calculated. From these values and those obtained previously, the temperature-coefficients of association have been calculated. Although different

substances were used for calculating the constants, the values of the association at the different fluidities are in close agreement. E. G.

Adsorption of Dissolved Substances. ERIK HÄGGLUND (*Zeitsch. physiol. Chem.*, 1910, **64**, 294—301).—Lagergren (*Bihang K. Svenska Vet.-Akad. Handl*, 1898) claims to have observed negative adsorption of sodium, potassium, ammonium, and magnesium chlorides and potassium and ammonium bromides when charcoal, kaolin, or glass powder were used. Negative adsorption could not be observed by Kellner (Abstr., 1896, ii, 232), van Bemmelen (Abstr., 1902, ii, 70; 1904, ii, 18), or Freundlich (Abstr., 1907, ii, 155). The author's results also contradict Lagergren's statement. The absorbents and solutions used were the same. J. J. S.

Dissociation of Hydrogen Bromide and Iodide at High Temperatures. II. KURT VOGEL VON FALCKENSTEIN (*Zeitsch. physikal. Chem.*, 1910, **72**, 113—116).—The experimental results for the dissociation of hydrogen bromide and iodide already published (compare this vol., ii, 27) are shown to be in excellent agreement with the values calculated by Nernst (*Zeitsch. Elektrochem.*, 1909, 18, 687) according to his theory. G. S.

Concentration of the Hydrogen Ions in Solutions of Phosphoric Acid and Sodium Hydroxide. WILHELM E. RINGER (*Chem. Weekblad*, 1910, **7**, 203—207).—An investigation of the extent of dissociation of the three phosphates of sodium in dilute solution. A. J. W.

Calcium Salts of Citric Acid and their Hydrolytic Changes. A. PARROZZANI (*Chem. Zentr.*, 1910, i, 514; from *Staz. sperim. agrar. ital.*, 1909, **42**, 965—998).—The author shows that solutions of monocalcium citrate have a tendency to form dicalcium citrate and free citric acid on hydrolysis, and the latter, even in presence of the free acid, changes into tricalcium phosphate. The more dilute the solution and the higher the temperature, the greater the amount of change. The barium salts are more stable than those of calcium. The author has determined the dissociation constants of mono- and di-calcium citrates, and shows that these values increase with increasing concentration and temperature. S. B. S.

Coloration of Solutions of Nitrophenols. WASSILI W. SCHARWIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 237—249).—The author has measured the depths of colour of various series of solutions of *o*- and *p*-nitrophenols in order to ascertain whether the increase of colour on dilution follows Ostwald's ionisation law, such increase of colour being due, according to Hantzsch (Abstr., 1906, i, 353), to gradual conversion of undissociated nitrophenol into the dissociated coloured *aci*-form.

It is found that solutions of *o*- or *p*-nitrophenol in commercial spirit obey the law: $\beta/V(1-\beta)=K_1$, where β is the ratio of the colour of a solution of dilution V to the colour of an infinitely dilute solution, and

K_1 is a constant; this law holds for *o*-nitrophenol from a dilution of 150 to 4000 litres per mol., and for the *p*-compound from 1 to 1200 litres.

Aqueous solutions of the two nitrophenols exhibit depths of colour increasing with dilution according to the law: $\beta^2/V(1-\beta)=k$, the curves showing the relations between colour and dilution being identical with those expressing the variation of electrical conductivity with dilution. The conductivity for the dilution nV can hence be calculated by means of the equation: $\mu_{nV}=\mu_V C_{nV}/C_V$. Similar variations of the depth of colour and conductivity are exhibited by absolute alcoholic solutions of *o*-nitrophenol. The reason for the colour of solutions in commercial alcohol following a different law may lie in the presence of some admixture, such as traces of alkali dissolved from the glass, in the solvent.

Similar changes of the colour with dilution are shown by alcoholic solutions of alizarin, with which not only the depth, but also the nature, of the colour alters. If the alkali salts of alizarin (violet) are regarded as being derived from the quinonoid formula

$$C_6H_4{<}{\substack{C(OM)\\C(OM)}}{>}C_6H_2{<}{\substack{O\\O}}$$

(compare Perkin, Trans., 1899, **75**, 433), the changes in colour of alizarin solutions are best explained by the existence of the tautomeric yellow form, $C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2(OH)_2$. With solutions of the nitrophenols, also, the absorption spectrum varies with the depth of colour on dilution, but the variation is too small to interfere with the colorimetric measurements. T. H. P.

The Theory of Cohesion Pressure (Surface Pressure) and the Processes of Resorption, Especially in the Alimentary Tract. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1910, **24**, 322—340).—A reply to Török and to Buglia. The author reiterates his theory that osmosis is governed by the cohesion pressures of solutions. He applies the theory to consideration of the passage of substances through a membrane. The more a substance diminishes the surface tension of a solution, the less its cohesion pressure; the cohesion pressure of the same solutions on different sides of a membrane can be different if the sides of the membrane itself are chemically or physically different; the direction and rate of osmosis is a function, not only of the cohesion pressure of diosmosing substances, but also of the cohesion pressure at or in a membrane, or, in other words, the difference of the surface tensions between a membrane and the constituents of the solutions. He seeks to obtain confirmation of his theory from the researches of Adrian Brown on the osmosis into barley grains of various solutions, and the researches of Hedin, Katzenellenbogen, Török, and Buglia on the resorption in the alimentary tract of various solutions, and influence of additions to the same of substances which lower the surface tension. The author seeks to explain the deviations from his theory in the results of Török and Buglia by the fact that the intestinal membranes contain a large amount of lipoid material which has already greatly lowered the surface tension of the intestinal juices. Further addition

of substances which act physically in the same way has comparatively little effect. Experiments are quoted in support of this statement.

S. B. S.

Physical Properties of Solutions. I. ADOLF HEYDWEILLER (*Ann. Physik*, 1910, [iv], **31**, 1063—1064).—It is pointed out that the relationship between the density and electrical conductivity of aqueous salt solutions, indicated by the author in a recent paper (this vol., ii, 106), has been previously obtained in a somewhat different form by Magie (*Physikal. Rev.*, 1907, **25**, 171).

H. M. D.

Absolute Sulphuric Acid as Solvent. FRIEDRICH BERGIUS (*Zeitsch. physikal. Chem.*, 1910, **72**, 338—361. Compare Hantzsch, Abstr., 1908, ii, 14, 462; 1909, ii, 18, 973).—The change of molar conductivity with dilution has been determined at 25° for a number of salts and acids in perfectly anhydrous sulphuric acid in a rather complicated apparatus, which is figured and described in detail. According to the nature of the solute, the molar conductivity, μ_v, may increase, diminish, or remain constant on dilution.

For potassium sulphate, μ_v remains constant at 75° for solutions varying in concentration between 0·0046 and 0·085*N*. When a little water is added, μ_v diminishes somewhat with dilution. For sodium sulphate, μ_v increases slightly with increased concentration; for the corresponding rubidium salt, μ_v diminishes at first with increasing concentration, attains a minimum value, and then increases. For nitric acid, μ_v diminishes gradually from 178·8 to 137·7 as the concentration increases from 0·0266 to 0·1731*N*. For dichloroacetic acid, μ_v is small, and increases with the concentration. For *p*-toluenesulphonic acid with $4H_2O$, μ_v increases with the concentration; for the same acid with $1H_2O$, μ_v attains a minimum value in 0·06*N*-solution. μ_∞ for sulphur trioxide increases, and for water diminishes, with the dilution.

The conductivity of a saturated solution of potassium sulphate in sulphuric acid has been measured in a special form of apparatus. The solution is 3·1 normal at 25°, and μ_v is 17·4.

In the course of the experiments a number of compounds of sulphates with sulphuric acid have been obtained: $K_2SO_4,6H_2SO_4$, m. p. 55°; $Na_2SO_4,8H_2SO_4$, m. p. 40°, and $Li_2SO_4,7H_2SO_4$, m. p. 12°, are crystalline. The composition of the following compounds: $Rb_2SO_4,6H_2SO_4$; $SrSO_4,14H_2SO_4$, and $BaSO_4,30H_2SO_4$, has been determined by analysis of their saturated solutions.

Some potential measurements in sulphuric acid solution did not give satisfactory results. The viscosity coefficient of absolute sulphuric acid is 0·1915 at 25°.

The abnormal values of μ_v are ascribed to complex formation between solvent and solute.

G. S.

Energy Relations of Solute and Solvent. M. M. GARVER (*J. Physical Chem.*, 1910, **14**, 260—270).—The author considers that the nomenclature attaching to the theory of osmotic pressure is inconsistent with experimental facts. Osmotic pressure has no

significance or existence, except as the hydrostatic pressure produced by osmosis through semi-permeable septa. From a consideration of the activity of the solvent, an equation of the form $(p_1 - p_2)/p_1 = (P_1 - P_2)/P_1$ is derived, in which p_1 and p_2 are the vapour pressures of the solvent and solution, and P_1 and P_2 are the so-called intrinsic pressures of the liquid solvent as such and when mixed with the dissolved substance. The intrinsic pressure is a measure of the activity of the solvent. H. M. D.

Partition Law in Mixed Solvents. WALTER HERZ and ALFRED KURZER (*Zeitsch. Elektrochem.*, 1910, **16**, 240—242).—The partition of iodine between water and mixtures of carbon disulphide and carbon tetrachloride, of ammonia between water and mixtures of chloroform and amyl alcohol, of oxalic acid between water and mixtures of ethyl ether and amyl alcohol, and of acetic acid between mixtures of carbon disulphide and carbon tetrachloride is measured.

In the first two cases the ratio of the concentrations in the two liquid phases is constant; in the case of oxalic acid, a constant ratio exists for the undissociated part of the acid, and in the case of acetic acid the square root of the concentration in the non-aqueous phase is taken.

A mixture of two solvents therefore behaves in exactly the same way as a homogeneous liquid. T. E.

Mixed Crystals or Solid Solutions. ST. RUŽIČKA (*Zeitsch. physikal. Chem.*, 1910, **72**, 381—382).—According to van't Hoff, mixed crystals are to be regarded as solid solutions, and diffusion should therefore take place in the crystals. Lehmann (*Ann. Phys. Chem.*, 1894, [iii], **51**, 67) tested this suggestion by placing thin crystals of meconic acid, intensely coloured with a violet colouring matter, in light petroleum, in which the colouring matter is readily soluble, but found after a prolonged period that the colouring matter was not extracted from the crystals. Ostwald (*Zeitsch. physikal. Chem.*, 1894, **13**, 758) pointed out that this investigation would only be conclusive if meconic acid did not take up the colouring matter from its solution in light petroleum. The author has tested this suggestion, and finds that even after five weeks no trace of colour is taken up by the crystals. Hence the conclusion is drawn that diffusion does not take place in such crystals. G. S.

Proof of the Crystalline Nature of "Amorphous" Precipitates and Condensation Methods for the Preparation of Disperse Systems. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 209—213).—When a crystal of Glauber's salt is immersed in a saturated solution of barium chloride, the formation of definitely crystalline particles of barium sulphate is observed. On the other hand, when crystals of barium chloride are placed in a saturated solution of sodium sulphate, the precipitated barium sulphate is "amorphous." The difference in behaviour is attributed to the difference in the osmotic pressures of the saturated solutions of the two substances. In the former case the conditions are such that a slow,

steady process of diffusion can take place through the membrane of barium sulphate which is first formed. In the second case this is impossible by reason of the unfavourable direction of the osmotic pressure gradient.

The second part of the paper is devoted to a theoretical discussion of the factors which are of influence in the formation of disperse systems by processes of crystallisation and liquefaction. H. M. D.

Colloidal Ice. P. P. von Weimarn and Wolfgang Ostwald (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 181—192).—The paper contains separate communications by the two authors on the formation of colloidal ice.

von Weimarn's experiments show that a colloidal suspension of ice is obtained when a saturated solution of water in ethyl ether is cooled by means of liquid air. When the vessel containing the opalescent suspension of ice is removed from the cooling bath, rapid coagulation takes place, and a flocculent precipitate of ice is the result. Other solvents can be employed instead of ethyl ether.

The phenomena observed when water is mixed with liquid air are described, and it is shown that the disperse character of the ice suspension is dependent on the velocity of the process of condensation.

In Ostwald's experiments, solutions of water in chloroform were cooled to $-20°$. The nature of the colloidal suspensions of ice which are thus obtained is found to be dependent on the concentration of the water in the chloroform solution, and on the rate of cooling. Various substances, such as salts of the higher fatty acids, caoutchouc, colophony, and mastic, are found to act as protective colloids. In presence of small quantities of these substances, colloidal suspensions of a more highly disperse character are obtained, and these are more stable than the suspensions which are obtained under otherwise similar conditions in the absence of these protective colloids. H. M. D.

Nomenclature of Pseudo-Systems. Hugo R. Kruyt (*Chem. Weekblad*, 1910, **7**, 133—136).—The author adduces arguments in support of the contention that the nomenclature put forward by him for systems in which sulphur is a component is superior to that suggested by Roozeboom and Aten (Abstr., 1905, ii, 803; compare also Kruyt, Abstr., 1908, ii, 1028; 1909, ii, 228, 802; Aten, Abstr., 1909, ii, 971). A. J. W.

Allotropy and Internal Equilibrium. Andreas Smits (*Chem. Weekblad*, 1910, **7**, 155—166. Compare this vol., ii, 195).—An application of the principle that in a system of substances at constant temperature and pressure the thermodynamic potential is a minimum. A. J. W.

Theory of the Phenomenon of Allotropy. Andreas Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **12**, 763—774. Compare this vol., ii, 195, and preceding abstract).—According to the author's theory, the different forms exhibited by certain substances in the solid state may be due to the existence of two modifications in dynamic equili-

brium. The various types which the concentration temperature equilibrium diagrams assume when this assumption is made are considered in detail, and observations relating to the different forms of mercuric iodide, sulphur, and phosphorus are cited in favour of the applicability of the theory in these special cases. H. M. D.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. Interaction of Mixed Salt Solutions and Liquid Amalgams. I. Study of the Reaction $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m-n)Hg$. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1910, **32**, 502—507).—In an earlier paper (Abstr., 1907, ii, 463) it has been shown that liquid amalgams of the alkali metals are solutions in mercury of compounds of the general formula MHg_m, and that a solution of sodium and potassium chlorides reacts readily with either sodium or potassium amalgam with the rapid establishment of an equilibrium. A further study has now been made of these reactions. It has been found that in the reversible reaction: $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m-n)Hg$, the equilibrium constant $= 0.315$. From the results obtained previously (Abstr., 1908, ii, 38) on the action of mixed sodium and rubidium, and sodium and cæsium chloride solutions on sodium and rubidium, and sodium and cæsium amalgams respectively, the equilibrium constant for the reaction: $MHg_m + Na^{\cdot} \rightleftarrows NaHg_n + (m-n)Hg + M^{\cdot}$ has been calculated, and found to be 0·31, 0·37, and 0·48, when M represents K, Rb, and Cs in the order named.

The results of this investigation confirm the conclusions that, at any definite concentration, salts of the same ionic type have the same degree of ionisation, and that the degree of ionisation of each salt in a mixture, such as that of potassium and sodium chlorides, in which there is a common ion, is the same as if that salt alone was present with an ion concentration equal to the sum of those of the separate salts (compare Noyes, Abstr., 1908, ii, 347; and Noyes and Johnston, Abstr., 1909, ii, 854). These conclusions are shown to be valid even in the case of very concentrated solutions. E. G.

Equilibrium in the System Mercuric Chloride–Pyridine. RUSSEL S. MCBRIDE (*J. Physical Chem.*, 1910, **14**, 189—200).—Solubility and melting-point measurements have been made which determine the limits of existence of the three compounds:

$$HgCl_2,2C_5H_5N,$$

$HgCl_2,C_5H_5N$, and $3HgCl_2,2C_5H_5N$.

The first two compounds are connected by a transition temperature at 76°, and the second and the third by a transition temperature at 106·2°. A metastable transition point at 94·7° connects the first and the third compound. The first two compounds melt respectively at 96° and 120°, but these melting points are in the metastable region. It seems probable that there is a further compound which only exists below −22°, but its composition has not been determined.

H. M. D.

Theory of Periodic Reactions. ALFRED J. LOTKA (*J. Physical Chem.*, 1910, **14**, 271—274; *Zeitsch. physikal. Chem.*, 1910, **72**, 508—511).—By the application of the law of mass action to the case

of a chemical change which takes place in a series of stages, and in which the consecutive reactions are auto-catalytically accelerated by the decomposition products formed, it is found that the conditions requisite for a periodic reaction are obtained. H. M. D.

Influence of the Medium on Reaction Velocity. Nikolaï Schiloff and A. Pudofkin (*Zeitsch. Elektrochem*, 1910, **16**, 125—129).—The rate of oxidation of hydriodic acid by hydrogen peroxide in presence of sulphuric acid is measured in mixtures of ethyl or methyl alcohol and water. In both cases a minimum velocity is observed at 40 to 50% alcohol. The velocities in 90% methyl and ethyl alcohol are almost the same, and nearly three times the velocity in pure water. Up to 70% of alcohol, the reaction follows the equation of the second order. It is of interest that the viscosities of mixtures of methyl and ethyl alcohol with water also pass through maxima at 40 and 50 per cent. respectively. T. E.

Velocity of Reactions in a Heterogeneous System. R. L. Espil (*Bull. Soc. chim.*, 1910, [iv], **7**, 155—158).—A physico-chemical study of the reaction $6KOH + (2n+1)Se = 2K_2Se_n + K_2SeO_3 + 3H_2O$. The influence of time, concentration, and temperature on the velocity of reaction was examined, and the conclusion drawn that the system obeys Berthelot's law for homogeneous systems. W. O. W.

Free Energy of Chemical Action in Mixtures of Glycerol with Alcohols. Leo Pissarjewsky and P. Trachoniotowsky (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 249—295. Compare Abstr., 1909, ii, 866).—The authors have measured the constant $K = C_{Ag(CN)'_2}/C_{Br'}$ of the reaction $2AgCN + KBr \rightleftarrows AgBr + KAg(CN)_2$ at 25° and 45° in various mixtures of glycerol, ethyl and methyl alcohols, and water.

At 25° the addition of methyl alcohol to glycerol is accompanied by an increase of K, and when the alcohol constitutes more than 50% of the mixed solvent, the reaction becomes non-reversible instead of reversible. The addition of methyl alcohol to water also increases K, but to a less degree, and even with 75% of the alcohol the reaction is still far from proceeding to an end. The addition of water to glycerol should, consequently, diminish K, and this is found to be the case. The addition of ethyl alcohol (50%) to water produces a slight increase (8—9%) in the value of K, whilst by the addition of 50% of glycerol, K is increased 2·4 times. The increase in K caused by addition of ethyl alcohol to glycerol is far less than that brought about by methyl alcohol.

At 45° the reaction is non-reversible in glycerol containing 50—88% of methyl alcohol, but is reversible with 88—100% of the alcohol. When the reaction is practically irreversible, the diminution of free energy does not exceed about 3000 calories. At 45° the addition of ethyl alcohol to glycerol causes a greater change in the value of K than at 25°, the reaction being irreversible in presence of 50% of the alcohol.

Comparison of the values of K and of the heat effect (A) in all the solvents with those of the internal friction fails to reveal any definite relationship between η and A or K. In these different mixed solvents, the heat effect cannot be regarded as even an approximate measure of the maximal work and affinity directing the reaction to the one side or the other. T. H. P.

Theory of the Inversion of Sucrose. JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1910, **72**, 117—123).—Bodenstein (*Zeitsch. Elektrochem.*, 1909, **15**, 413) and Hudson (compare Abstr., 1908, i, 605) have suggested that the relatively high velocity found by the author during the earliest stage of the hydrolysis of sucrose in the presence of acids (compare Abstr., 1908, ii, 265) is due to experimental error, but the author maintains the accuracy of his work. The experiments on the mutarotation of lævulose have been repeated, and the values now found are in fair agreement with those of previous observers. G. S.

Correction of the Apparent Weight of a Salt to the Vacuum Standard. THEODORE W. RICHARDS and GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1910, **32**, 507—512*).—It has been stated by Guye and Zachariadès (Abstr., 1909, ii, 989) that the usual correction for reducing a weighing to the vacuum standard is always too high on account of the adsorption of gases by the substance, and is therefore liable to introduce serious error. Scott (Proc., 1909, **25**, 286), however, has been unable to find any important amount of adsorption, even in finely-powdered potassium chloride.

In the present paper it is pointed out that, contrary to the suggestion of Guye and Zachariadès, the possibility of adsorption of gases by solids was not overlooked in the recent investigations on atomic weights which have been carried out at Harvard. Experiments are described which indicate that the conclusions arrived at by Guye and Zachariadès are inaccurate. E. G.

Practical Rules for Correcting Numbers, especially in Changing to Another System of Atomic Weights. FRIEDRICH KOHLRAUSCH (*Zeitsch. physikal. Chem.*, 1910, **72**, 43—48).—Some simple formulæ are given to facilitate the correction of experimental numbers when some of the factors on which the numbers are based are altered. Such corrections were necessary, for example, for the numbers expressing the molecular conductivity of electrolytes when a large number of atomic weights were slightly altered in the International Table for 1909. The formulæ are only valid for small corrections, and the mode of applying them is illustrated by examples. G. S.

* and *Zeitsch. anorg. Chem.*, 1910, **66**, 418—425.

Inorganic Chemistry.

Atomic Weight of Hydrogen. GRINNELL JONES (*J. Amer. Chem. Soc.*, 1910, **32**, 513—517).—The results obtained in the determination of the atomic weight of hydrogen by physico-chemical methods are collected and compared with those obtained by chemical methods. In some cases the results have been re-calculated with the most trustworthy data for the density of hydrogen and oxygen, and other corrections have been applied when necessary. All the physico-chemical results fall within the limits of the best chemical data. The results obtained by various workers by the method of limiting density show remarkable agreement, and indicate that the compressibility data are very accurate. The conclusion of Noyes (Abstr., 1908, ii, 367) that 1·00775 is the most probable value for the atomic weight of hydrogen (O = 16) is confirmed. E. G.

Colloidal Ice. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 226—230).—When cooled in liquid air, saturated solutions of a number of thiocyanates, chlorides, sulphates, and other salts are converted completely into solid, transparent, glassy masses, the water not crystallising out in spite of the low temperature (− 190°); so that it is necessary to assume the existence of liquid water at − 190°, and to conclude that these glassy masses represent solid, suspensoid solutions with quite a high degree of dispersion. T. H. P.

Phenomena Observed on Mixing Liquid Air with Water. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 230—232).—When water is poured on to the surface of liquid air containing a large excess of oxygen, it does not solidify immediately, but at first assumes a semi-solid consistency. When liquid air is poured into water, the bluish drops in some cases fall to the bottom and in others rise to the surface, and become surrounded by atmospheres of gaseous air and thin elastic scales of ice. The water finally solidifies to a turbid, porous system; so that ice, as well as any other substance, for example, barium sulphate, may be obtained as precipitates of varying form and degree of dispersion, according to the rapidity of condensation. Condensed gases are very suitable dispersive media for obtaining such suspensoids. T. H. P.

The Measurement of the Hydrogen Ion Concentration in Sea-water. SÖREN P. L. SÖRENSEN and S. PALITZSCH (*Biochem. Zeitsch.*, 1910, **24**, 387—415).—The estimations were made by the colorimetric method already described by Sörensen, nitrophenol, neutral-red, and phenolphthalein being the indicators employed. Corrections for the alteration of the changing point of the indicator, due to the salts, were made by comparing the hydrogen ion concentrations estimated colorimetrically with those estimated electrically by concentration in solutions containing 20—35% of salts (or sea water),

from which the carbon dioxide had been expelled by hydrogen. The exponent of the hydrogen ion concentrations found in sea-waters taken from different localities and depths varied between $p = 6{\cdot}6$ and $8{\cdot}6$. It is not certain how far these variations are due to the alkalinity of the glass of the vessels in which the samples were preserved.

S. B. S.

The Alkalinity of Sea-water. ERNEST RUPPIN (*Zeitsch. anorg. Chem.*, 1910, **66**, 122—156).—See this vol., ii, 452.

Laboratory Apparatus for the Preparation of Fluorine. I. GINO GALLO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 206—212).—This apparatus for the electrolysis of anhydrous hydrogen fluoride consists essentially of a platinum crucible, connected with the negative pole of the current generator, and sealed with a sulphur cover, from the lower surface of which a small platinum cylinder, closed at the bottom but perforated laterally, projects nearly to the bottom of the crucible. Near its upper end, this cylinder contains a disk of fused potassium fluoride traversed by a thick platinum wire, connected with the positive pole, and arranged in the form of a spiral near the bottom of the cylinder, and by a gas delivery tube. The space between the potassium fluoride and the sulphur is filled up with a thin layer of calcium fluoride and fused sulphur. A second gas delivery tube passes through the sulphur cover into the crucible. Such an apparatus permits of the electrolysis of small quantities (5 grams) of anhydrous hydrogen fluoride. T. H. P.

Attempt to Prepare Oxygenated Compounds of Fluorine. II. GINO GALLO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 295—299).—An attempt to prepare an oxygen compound of fluorine by subjecting a mixture of the two gases to the action of an electric discharge in an apparatus similar to that employed for the preparation of ozone, resulted in an explosion and fracture of the apparatus. T. H. P.

The Action of Liquids which Dissolve Sulphur on Metallic Sulphides. EDUARD JORDIS and EUGEN SCHWEIZER (*Zeitsch. angew. Chem.*, 1910, **23**, 577—591).—Sulphides prepared by precipitation with ammonium sulphide under different conditions, and washed out of contact with air, have been either extracted while wet with carbon disulphide, or dried in an atmosphere of carbon dioxide, or dried and fused in a closed tube, and then extracted. Sulphides prepared by melting the metals with sulphur and native minerals have also been studied. A specially modified form of Soxhlet's extraction apparatus is used, and the exhaustion is continued for fifty to a hundred hours. The sulphur is estimated after oxidation with bromine. Blank experiments prove that sulphur is not obtained from the carbon disulphide under such conditions.

Cupric sulphide always contains some "free" sulphur, which is removed by solvents. Its quantity varies with the temperature to which the sulphide has been exposed, being greatest in the sulphide precipitated from hot solutions, although the absolute quantity of sulphur in such precipitates is less. The higher the boiling point of

the solvent, the greater is the quantity of sulphur extracted. Nickel and ferrous sulphides behave similarly. Ferric sulphide, precipitated by ammonium sulphide from a ferric salt, gives up sulphur to solvents until the sulphur content is rather less than that of ferrous sulphide. In the presence of water, the whole of the sulphur may be extracted, leaving ferric hydroxide. Prepared in the dry way, ferrous sulphide is formed at once and quantitatively, whilst the quantity of sulphur required to form ferric sulphide is only taken up slowly on continued heating. Native marcasite is very stable.

Generally, sulphides prepared by precipitation contain both water and sulphate, even when dried. Those prepared by fusion approach more nearly to the composition MS_n. Sulphide hydrosols contain more sulphur than the solid substances. In investigating the equilibrium between solutions of metallic salts and hydrogen or ammonium sulphides, it is necessary to analyse the solid phase in each case, and not to assume that a sulphide is formed in stoicheiometric proportions.

C. H. D.

Behaviour of White Phosphorus at Low Temperatures. ERSNT COHEN and KATSUJI INOUYE (*Chem. Weekblad,* 1910, 7, 277—291. Compare Giran, *J. Phys.*, 1903, [iv], 2, Nov.).—The authors find that Giran's solubility curve for white phosphorus in carbon disulphide is incorrect; that the phenomena observed by him afford no justification for the assumption of the formation of a compound of $12P + CS_2$; and that there is no experimental evidence in support of the existence at low temperatures of a hitherto unknown allotropic modification of white phosphorus.

A. J. W.

A Colloidal Solution of Pure Elemental Arsenic. LECOQ (*Compt. rend.*, 1910, 150, 700—702).—Colloidal arsenic obtained by Auger's process (Abstr., 1907, ii, 948) is contaminated with salts from which it is difficult to purify it. A solution of the pure substance may be obtained by electrolysing an alkaline solution, using an anode of arsenic, or, better, by the electrolytic reduction of a solution of 3 grams of arsenious oxide in a litre of 0·3% sodium hydroxide. A current of 2—3 amperes and 100 volts should be employed, using a platinum cathode and a mercury anode. The solution is cooled during electrolysis and purified by dialysis. The addition of a trace of gum renders the colloid much more stable.

A solution prepared in this way appeared deep brown, and was found to contain, on analysis, about 0·07% of arsenic.

W. O. W.

Reduction of the Chlorides of Arsenic and Boron by Hydrogen under the Influence of the Electrical Discharge. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, 150, 872—874. Compare this vol., ii, 121).—When a mixture of the vapour of arsenious chloride and hydrogen is treated by the method already described, a brown deposit is formed on the tube, having a composition represented by $As_{11}Cl$ and consisting probably

of a mixture of arsenic with an unknown subchloride. Under similar conditions, boron trichloride is reduced to boron, but no evidence of the formation of a lower chloride was obtained.

W. O. W.

The Influence of Chlorides on the Solubility of Boric Acid. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **66**, 358—360. Compare Rothmund and Wilsmore, Abstr., 1902, ii, 447).—The influence of chlorides on the solubility of boric acid follows the order of the electro-affinity of the cations. Hydrogen, lithium, and sodium chlorides lower the solubility, potassium and rubidium chlorides raise it. These results indicate that hydration of the cations is insufficient to explain the effects.

C. H. D.

Vapour Pressure and Velocity of Dehydration of Powdered Silicic Acids. GUSTAV TSCHERMAK (*Zeitsch. anorg. Chem.*, 1910, **66**, 199—205. Compare Abstr., 1909, ii, 884; van Bemmelen, Abstr., 1908, ii, 838).—The curves showing the velocity of dehydration of silicic acids change abruptly in direction at certain compositions, $SiO_2 : nH_2O$. For olivine and chabasite, $n = 1$; for heulandite, $n = 0{\cdot}83$, or 5 : 6; for labradorite, $n = 0{\cdot}60$ or 3 : 5. The method of determining the vapour tension is less suitable than the dynamic method for detecting discontinuities, but yields results which are consistent with the latter.

C. H. D.

Tschermak's Silicic Acids. AURELIO SERRA (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 202—205).—The study of the drying curve of the silicic acid obtained from leucite by the action of hydrochloric acid (compare Tschermak, Abstr., 1905, ii, 816; 1906, ii, 771; Baschieri, Abstr., 1909, ii, 589) gives the following results. The temperature at which the mineral is decomposed by the acid, and that at which the silicic acid is kept until of constant weight, the quantity and concentration of the hydrochloric acid employed to decompose the leucite, all exert considerable influence on the composition of the silicic acid obtained. The proportion of water in the latter varied from 20% to 31·80%, so that the ratio of H_2O to SiO_2 varies between 1 : 1·19 and 1 : 0·64, the corresponding limiting formulæ of the silicic acid from which leucite must be regarded as derived being $H_{10}Si_6O_{17}$ and $H_6Si_2O_7$.

T. H. P.

Laws of Convergent Combustion. JEAN MEUNIER (*Compt. rend.*, 1910, **150**, 781—783. Compare Abstr., 1908, ii, 463; 1909, ii, 311).—The author describes new observations relating to the phenomenon of combustion without flame, and these are said to support the view that the combustion is attended by a convergence of the molecules to the ignition point. With platinum wires of different diameters and a constant supply of coal gas, it is found that the intensity of the incandescent combustion process varies inversely as the diameter of the wire. For a given wire, the intensity of the incandescence increases with the explosive character of the gaseous mixture which surrounds it.

The phenomenon is not confined to platinum surfaces; it is also observable with other substances, but these require a preliminary heating to a higher temperature than is necessary in the case of platinum. Next to platinum, the effects are exhibited most readily by nickel. Reference is made to the application of the observations in connexion with the incandescent mantle industry. H. M. D.

Carbon Monosulphide. Sir JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1910, **83**, *A*, 408—413).—Thiocarbonyl chloride reacts rapidly at the ordinary temperature with nickel carbonyl according to the equation. $x\mathrm{CSCl_2} + x\mathrm{Ni(CO)_4} = x\mathrm{NiCl_2} + 4x\mathrm{CO} + (\mathrm{CS})_x$. The nickel chloride produced in the reaction is extracted by water, leaving a brown, solid substance, which analysis indicates to be a polymeric form of carbon monosulphide. The reaction also takes place, although less rapidly, at $-20°$, and the same result is obtained when the reacting substances are dissolved in dry ether, light petroleum, carbon tetrachloride, or chloroform. Even when the reacting liquids are carefully dried over phosphoric oxide, the carbon monosulphide is still obtained. The purification of the substance is rendered difficult by the fact that it retains water and thiocarbonyl chloride with great persistence. To remove these as far as possible, the product obtained after extracting with water in a Soxhlet apparatus was dried by heating at 100°, and then at 150° or 200°, under reduced pressure.

The finely-divided substance has D about 1·6; after compression into a solid block, the value 1·83 was obtained. The molecular volume is therefore 24, which is about 10% greater than the sum of the atomic volumes of its constituents.

Carbon monosulphide is not altered by dilute sulphuric acid, but with the concentrated acid it gives a purplish-brown solution, the colour of which is slowly destroyed at the boiling point when carbon dioxide and sulphur dioxide are evolved. When the purplish-brown solution is poured into water, unchanged carbon monosulphide is precipitated. It is dissolved by concentrated nitric acid at the ordinary temperature, giving a red solution, the colour of which is only slowly destroyed on heating. It dissolves in aqueous or alcoholic solutions of ammonia, ammonium sulphide, and potassium hydroxide, sulphide and hydrosulphide, giving deep brown solutions, from which acids precipitate the carbon monosulphide unchanged.

When heated in a good vacuum, no change takes place below 360°, except the liberation of a small quantity of hydrogen sulphide; at a low, red heat, carbon disulphide is formed according to $2(\mathrm{CS})_x = x\mathrm{C} + x\mathrm{CS_2}$. When heated in a current of dry hydrogen, hydrogen sulphide is evolved; when heated in dry chlorine, sulphur is evolved.

It seems probable that the red substance obtained by long exposure of carbon disulphide to sunlight is also a polymeric form of carbon monosulphide. H. M. D.

Change of Carbon Disulphide into a Gaseous Product Condensible and Explosive near the Temperature of Liquid Air. Sir JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1910, **83**, *A*, 526—529. Compare preceding abstract).—When carbon

disulphide vapour at low pressure is subjected to the action of the silent electric discharge, it appears to be decomposed with formation of sulphur and gaseous carbon monosulphide. When the gas resulting from the discharge tube is passed through a tube cooled by liquid air, the monosulphide is condensed along with the unchanged disulphide. If the condensing tube is removed from the liquid air and its temperature allowed to rise, the monosulphide polymerises with explosive violence to form the brown, solid substance, $(CS)_x$, previously described. In presence of excess of carbon disulphide vapour, the gaseous monosulphide appears to be fairly stable under certain conditions. Some of it is still present after passing the product from the "ozoniser" through a tube immersed in boiling sulphur, or even through a short length of red-hot tube. It is, however, completely destroyed by passing through 10 cm. of a red-hot tube loosely packed with asbestos. The stability at high temperatures is consistent with the behaviour of an endothermic substance. At the ordinary temperature the gaseous monosulphide polymerises rapidly, even at low pressure and in presence of a large excess of carbon disulphide. H. M. D.

Viscosities of the Gases of the Argon Group. A. O. RANKINE (*Proc. Roy. Soc.*, 1910, *A*, **83**, 516—525).—The experimental method has been previously described (compare this vol., ii, 188). The viscosities, relative to that of air, are: helium 1·086, neon 1·721, argon 1·221, krypton 1·361, xenon 1·234. As the atomic weight increases, the viscosity increases and decreases in successive steps of gradually diminishing magnitude. By application of the kinetic theory, the author deduces the relative mean free paths, molecular volumes, and atomic densities, and compares these values with the relative atomic weights and viscosities. As the atomic weight of the inert element increases, the mean free path diminishes. By graphical representation of the connexion between these two quantities, it is found that the straight line joining the points representing helium and neon intersects the corresponding straight line for krypton and xenon close to the point which represents argon. With increasing atomic weight, the molecular volume increases, but there appears to be no simple general relationship between these two quantities.

H. M. D.

Solubility of Xenon, Krypton, Argon, Neon, and Helium in Water. ANDREAS VON ANTROPOFF (*Proc. Roy. Soc.*, 1910, **83**, *A*, 474—482).—Measurements of the solubility of the inert gases in water have been made at temperatures from 0° to 50°. Two series of values are given for krypton. At 20° the coefficients of absorption are: xenon 0·1109, krypton (1) 0·0788, krypton (2) 0·0670, argon 0·0379, neon 0·0147, helium 0·0138. Except in the case of helium and neon, the solubility shows a considerable increase with increasing atomic weight. The solubility of xenon is greater than that of any other gas which does not form a compound with the solvent. The solubility-temperature curves exhibit distinct minima; the minimum for xenon and argon lies at about 40°, that for krypton between 30° and 40°, for helium at about 10°, and there appears to be a minimum for neon in the neighbourhood of 0°. H. M. D.

The Solubility of Gases in Metals and Alloys. ADOLF SIEVERTS and WILHELM KRUMBHAAR (*Ber.*, 1910, **43**, 893—900. Compare Abstr., 1907, ii, 741; 1910, ii, 242, 1004).—The metals are heated in porcelain vessels, Meissen biscuit porcelain being impermeable to hydrogen at 1650°, and retaining a vacuum up to 1400°. A furnace with a short-circuited, cylindrical mass of amorphous carborundum, using 100—200 amperes at 12—20 volts, is used. The temperatures are read by means of a Wanner optical pyrometer.

Nitrogen is insoluble in most metals, but reacts with aluminium above 800° and with iron above 1200°, nitrides being formed. Carbon monoxide is quite insoluble in copper, but is absorbed by both liquid and solid nickel. Oxygen is insoluble in molten gold.

The solubility of sulphur dioxide in copper begins at the melting point, and increases with the temperature. On solidification, a large part of the dissolved gas is retained, but is recovered on heating in a vacuum. The solubility is proportional to the square root of the pressure.

Hydrogen is not dissolved by cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver, or gold. Copper, nickel, and iron dissolve it in the solid state, the solubility increasing in proportion to the temperature up to the melting point, and then increasing very rapidly, afterwards becoming again proportional to the temperature. In palladium, however, the solubility in the solid state is practically independent of the temperature, falling at the melting point to about half its value. The influence of pressure is the same as in the case of sulphur dioxide, and the rule also holds good for the solubility of oxygen in alloys of gold and silver.

The solubility of hydrogen in copper is unchanged by alloying with silver, is increased by alloying with nickel or platinum, and is diminished by alloying with gold, tin, or aluminium, the effect being proportional to the quantity of added metal in the range within which the constitution of the alloys remains unchanged. C. H. D.

Conversion of Halogens into the Alkali-metal Halogen Salts. JOSEPH MESCHORER (D.R.-P 217035).—It is found that a convenient method for preparing alkali halogen salts is the gradual treatment of a solution of sodium thiosulphate with sodium hydroxide and the required halogen in the proportions necessary for the equation:

$$Na_2S_2O_3 + 10NaOH + 8I = 8NaI + 2Na_2SO_4 + 5H_2O.$$

The sodium hydroxide may be replaced by sodium carbonate:

$$Na_2S_2O_3 + 5Na_2CO_3 + 8I = 8NaI + 2Na_2SO_4 + 5CO_2.$$

F. M. G. M.

Mixed Crystals of Silver Sulphate and Dichromate. RALPH G. VAN NAME and ROWLAND S. BOSWORTH (*Amer. J. Sci.*, 1910, [iv], **29**, 293—296).—Retgers was unable to obtain mixed crystals of silver sulphate and chromate. When these two salts, the former greatly in excess (99 : 1), are crystallised at a temperature of 25° from an acid solution (standard solution of sulphuric acid), there are obtained mixed crystals of sulphate and dichromate, ranging in colour from pale yellow to scarlet, and with the same orthorhombic form as the pure sulphate.

These crystals contain up to 4·1 mol. % of dichromate. When a greater proportion of chromate is present in the acid solution, only crystals of the pure dichromate separate. L. J. S.

Sulphates and Hydrogen Sulphates of Barium and Calcium. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1910, 66, 206—208).—Barium sulphate dissolves in hot concentrated sulphuric acid to a golden-yellow solution, which deposits the salt $BaH_2(SO_4)_2$ on cooling. This sulphate is readily decomposed by water, but is hydrated by a small quantity of water in a desiccator, setting to a hard mass: $BaH_2(SO_4)_2 + 2H_2O = BaH_2(SO_4)_2,2H_2O$. The sulphuric acid solution poured off from the first crop of crystals slowly coagulates to a gelatinous mass, rendered crystalline by the addition of water. Either gypsum or anhydrous calcium sulphate yields the salt $CaH_2(SO_4)_2$, which is also obtained in a gelatinous state. Decomposition with water yields the second anhydrous modification of calcium sulphate (this vol., ii, 125). C. H. D.

Preparation of Alkaline-earth Hydroxylaminedisulphonates. FRITZ RASCHIG (D.R.-P. 216747. Compare Divers, Trans., 1900, 77, 681).—When a milky suspension of calcium sulphite (obtained by treating calcium nitrite with calcium hydrogen sulphite) is cooled to 10°, N/10-sulphuric acid (or hydrochloric acid) stirred in, and the solution filtered, a clear solution of calcium hydroxylaminedisulphonate, $OH{\cdot}N(SO_3)_2Ca$, is obtained:

$$Ca(NO_2)_2 + 2Ca(HSO_3)_2 + 2HCl = 2OH{\cdot}N(SO_3)_2Ca + CaCl_2 + 2H_2O.$$

The calcium may be replaced by sodium in this reaction when sodium hydroxylaminedisulphonate is produced. F. M. G. M.

Action of the Alkali Nitrates on the Insoluble Carbonates. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 31—32. Compare Abstr., 1909, ii, 732).—The insoluble carbonate (0·2—0·3 gram) was treated with a solution of potassium or sodium nitrate (10 grams) in water (110 c.c.), the mixture heated to boiling, and boiled for a definite time, then cooled, and the clear filtrate tested, after evaporation where necessary, to determine whether any reaction had occurred.

Under these conditions, potassium nitrate reacts slightly with barium carbonate, but not with strontium carbonate in fifteen minutes. Sodium nitrate reacts with calcium carbonate (chalk) in fourteen minutes, with barium carbonate in sixteen minutes, with magnesium carbonate in sixteen minutes, with cadmium carbonate in seventeen minutes, with tricalcium phosphate in sixteen minutes, and with zinc carbonate in seventeen minutes. In the five former cases, only a faint, although definite, reaction is observed. With barium carbonate, the result is the same if the liquid is evaporated on a water-bath at 95—96° for four hours. Neither nickel carbonate, cobalt carbonate, nor lead carbonate is attacked by sodium nitrate in sixteen minutes, but lead carbonate is partly acted on in thirty-five minutes. E. H.

Preparation of a Double Salt of Zinc Hyposulphite with Sodium Sulphite. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 217038. Compare Abstr., 1908, ii, 185).—The addition of

sodium hydrogen sulphite to a solution of zinc hyposulphite leads to the formation of the double salt, $2ZnS_2O_4,Na_2SO_3$, which contains 75% ZnS_2O_4, and separates as a crystalline paste; after recrystallisation it is dried in a vacuum. F. M. G. M.

Thulium. CHARLES JAMES (*J. Amer. Chem. Soc.*, 1910, **32**, 517—518).—A considerable quantity of thulium bromate has been obtained by the repeated fractionation of the more soluble portions of rare earth bromates. This salt is more soluble than erbium bromate, but less so than ytterbium bromate. Thulium salts are pale bluish-green, but the colour is masked by minute quantities of erbium, and changes to yellowish-green, yellow, white, and finally pink as the amount of erbium increases. Some pure erbium has also been obtained, and both elements are being investigated. E. G.

Preparation of Aluminium as a Laboratory Experiment. BERNHARD NEUMANN and HJALMAR OLSEN (*Zeitsch. Elektrochem.*, 1910, **16**, 230—236).—A rectangular wrought iron box, 28 cm. square and 19 cm. deep, was used as the cell; a plate of Acheson graphite, 2·5 cm. thick, was placed on the bottom of the box and served as cathode. The anode consists of ordinary carbon (graphite conducts too much heat away and caused the bath to freeze on the surface): a convenient size is 10 cm. × 10 cm.; it is supported in such a way that it can be easily moved up and down. The experiment is begun by placing a piece of carbon (6 cm. long and 1·5 cm. diameter) between the electrodes, and surrounding it with the mixture of cryolite and alumina. About three and a-half hours are required to fuse 12 kilograms of mixture; during the fusion it is advisable to heat the bath by a gas burner below it, and to wrap it up in asbestos card. When the fusion is complete (a layer 2 cm. thick of solid always remains on the walls), the resistance carbon is withdrawn and electrolysis begun. The best results are obtained with a current density of 2 amperes per sq. cm. at the anode, and a bath containing 90% of cryolite and 10% of alumina; 8—10 volts are usually required, and the current efficiency rises as high as 70%.

The paper also contains a number of details of the management of the electrolysis. T. E.

Hydrolysis of Salts of the Cations $Al^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$. G. POVARNIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 207—213).—The author corrects some of the numerical data given in his previous paper (Abstr., 1909, ii, 1016), which were calculated by means of an inaccurate formula.

The discordant results obtained by different investigators for the proportion of aluminium sulphate hydrolysed at various dilutions are partly accounted for by the fact that special care was not taken to ensure the absence of the ions $K^{\cdot}$, $Na^{\cdot}$, and $NH_4^{\cdot}$, which exert a dehydrolysing influence (compare Denham, Trans., 1908, **93**, 41).

In general, chromic sulphate (a mixture of the green and violet modifications) is dehydrolysed by Na_2SO_4 and by $2NaCl$ to almost the same extent as is aluminium sulphate. T. H. P.

Indium. II. ALFRED THIEL and H. KOELSCH (*Zeitsch. anorg. Chem.*, 1910, **66**, 288—321. Compare Abstr., 1904, ii, 618).—Indium oxide, In_2O_3, loses weight on prolonged heating, and the effect is shown to be due to loss of oxygen, and not to volatilisation of the oxide. At very high temperatures, regular crystals and crystallites, photographs of which are given in the paper, are formed, consisting probably of an oxide, In_3O_4.

Indium may be estimated quantitatively by precipitation with ammonia and ignition of the hydroxide in a Gooch crucible at 850°. Freshly precipitated indium hydroxide is soluble in concentrated ammonia.

The only iodide hitherto known is the tri-iodide, InI_3. *Indium monoiodide*, InI, prepared by the action of iodine on an excess of the metal, and distillation at 700°, or by repeated distillation of the tri-iodide in hydrogen, is brownish-red. It is not decomposed by hot water, but in contact with air, oxidation takes place according to the equation: $2InI + 4H_2O + O_2 = 2In(OH)_3 + 2HI$. Sulphur dioxide converts it into indium sulphide, In_2S_3, and hydrogen sulphide into this sulphide and the tri-iodide.

It is not found possible to isolate indium di-iodide, InI_2, but the thermal analysis of mixtures of indium and iodine shows a maximum in the freezing-point curve at the composition InI_2, the maximum being raised by prolonged heating, indicating that the compound is only slowly formed from the mono- and tri-iodides.

Di-indium sulphide sublimes in flat plates. The *monosulphide*, InS, formed on heating the metal in hydrogen sulphide, is a soft, reddish-brown mass. Indium and selenium yield *indium selenide*, In_2Se_3, as a dark mass, and a lower selenide probably also exists. Indium and an excess of tellurium yield *indium telluride*, InTe, and probably a lower compound. Phosphorus vapour forms a compound approximating to the formula InP. C. H. D.

Electrolytic Production of Potassium Permanganate from Solutions of Potassium Manganate. PAUL ASKENASY and S. KLONOWSKI (*Zeitsch. Elektrochem.*, 1910, **16**, 170—176).—A solution containing 80 to 90 grams of potassium manganate per litre is electrolysed at 60° between iron electrodes, no diaphragm being used. The current density at the cathode is about 0·8 ampere per sq. cm., that at the anode is six or eight times smaller. In these circumstances the cathodic reduction is unimportant, and potassium permanganate soon crystallises out. When the quantity of electricity required theoretically for complete oxidation of the manganate has passed through the solution, it is found that nearly 60% of the manganate is oxidised; the loss of efficiency is due largely to the escape of free oxygen. By continuing the electrolysis, about 75% of the manganate can be converted; further oxidation is then balanced by the cathodic reduction. The results can be improved to some extent by using platinum electrodes and a diaphragm (at the expense of a double or treble voltage). More dilute or colder solutions give worse results.

T. E.

Electrolytic Preparation of Pure Iron. RICHARD AMBERG (*Zeitsch. Elektrochem.*, 1910, **16**, 125).—Remarks on a paper by Müller (Abstr., 1909, ii, 485). T. E.

Electrolytic Deposition of Iron. AUGUST PFAFF (*Zeitsch. Elektrochem.*, 1910, **16**, 217—223).—Three methods are tried: (1) a very concentrated solution of ferrous chloride, 0·03 to 0·04 ampere per sq. cm. cathodic current density, temperature 70°, electrolyte stirred (Merck, German patent 126839); (2) a saturated solution of ferrous ammonium sulphate at 30°, current density 0·01 ampere per sq. cm. (Burgess and Hambuechen, *Electrochem. Ind.*, 1904, **2**, 184); (3) a solution of ferrous sulphate saturated in the cold and containing sulphuric acid (about 0·05N), temperature 90°, current density 0·02 ampere per sq. cm, electrolyte stirred, and air excluded (H. Lee, *Diss.*, Dresden, 1906).

The experiments were always carried on for a considerable number of hours (twenty to one hundred and forty) in order to obtain a thick deposit. On the whole, the third set of conditions appeared to be the best, but none of the small modifications tried yielded a perfect deposit; even the best deposits contained pits or holes, owing to hydrogen bubbles adhering to them.

The addition of boric acid or ferric salts to the solution did not improve matters, but quite perfect deposits were obtained by blowing a current of air through the solution close to the cathode. This stirred the solution sufficiently, and removed the bubbles of hydrogen completely. The best conditions were found to be: a solution containing 0·01 equivalent of sulphuric acid and at least 2 equivalents of ferrous sulphate per litre at 70°, cathodic current density 0·02 ampere per sq. cm. Burgess's method, using the air current, also gave a deposit of perfect appearance, but it was extremely brittle. T. E.

Iron–Carbon Alloys. FRIEDRICH WÜST (*Zeitsch. Elektrochem.*, 1910, **16**, 190—191).—A continuation of the polemic with Heyn (this vol., ii, 298). T. E.

Action of Steam on Iron. J. A. NEWTON FRIEND (*J. West of Scotland Iron Steel Inst.*, 1910, **17**, 66—79. Compare this vol., ii, 39).—Iron is heated in a silica tube, immersed in a metal bath, a current of dry steam is passed, and the hydrogen evolved is collected over potassium hydroxide. Appreciable evolution of hydrogen begins at 400°, but the action begins perceptibly as low as 350°. With iron powder, which is contained in a silica tube having several small bulbs blown on it, the evolution begins at 240—280°, being lower the more finely the iron is powdered. The action probably takes place in three stages, namely, dissociation of steam, action of the oxygen thus liberated on iron to form ferrous oxide, and further oxidation to the magnetic oxide. C. H. D.

Ferrous Compounds of Nitric Oxide. II. WILHELM MANCHOT and F. HUTTNER (*Annalen*, 1910, **372**, 153—178. Compare Manchot and Zechentmayer, Abstr., 1907, ii, 93).—The object of

this investigation was to ascertain whether ferrous compounds, under suitable conditions, are capable of combining with more than one molecular proportion of nitric oxide for each atom of iron; the results obtained show that this is not possible.

The volume of nitric oxide absorbed by an aqueous solution of ferrous sulphate is diminished by the addition of small quantities of sulphuric acid, since the equilibrium represented by the equation:

$$FeSO_4 + NO \rightleftarrows FeSO_4,NO$$

is disturbed towards the left, but the volume of gas absorbed increases as the concentration of the acid increases, until a maximum is reached when the solution contains 82% of sulphuric acid; at this point and in solutions containing more than 82% of acid, each atomic proportion of iron is found to combine with one molecule of nitric oxide. The solutions under these conditions are cherry-red, and contain the complex *salt*, $FeSO_4,NO$, which has been isolated by adding a concentrated aqueous solution of ferrous sulphate saturated with nitric oxide to ice-cold concentrated sulphuric acid saturated with nitric oxide in an atmosphere of the same gas; it crystallises in small, red, stout leaflets and decomposes rapidly.

The action of hydrochloric acid is similar to that of sulphuric acid; the quantity of nitric oxide absorbed decreases at first, and then increases, until at a concentration of 34% of hydrogen chloride 1 mol. of nitric oxide combines with one atomic proportion of iron (compare Kohlschütter and Kutscheroff, Abstr., 1907, ii, 267).

The effect of the addition of phosphoric acid, calcium chloride, ammonium chloride, aniline hydrochloride, sucrose, gelatin, glue, egg-albumin, and serum to the solution of ferrous sulphate is in each case to decrease the proportion of nitric oxide absorbed.

Ferrous chloride dissolved in ethyl alcohol, ethyl acetate, ethyl benzoate, ethyl malonate, acetone, and pyridine absorbs one molecular proportion of nitric oxide. The solutions of the additive compounds of ferrous salts and nitric oxide in these solvents are green, with the exception of those in pyridine, which are reddish-brown.

The brown solution obtained by saturating an aqueous solution of ferrous sulphate with nitric oxide undoubtedly contains the compound $FeSO_4,NO$, and since the precipitates obtained by adding sodium hydroxide, sodium carbonate, sodium phosphate, and potassium ferrocyanide to the solution all contain nitric oxide, it follows that this substance has the constitution $NO\cdot Fe{:}SO_4$. The complex *salt*,

$$Fe(NO)SO_4,FeSO_4,13H_2O,$$

has been obtained by adding a saturated solution of nitric oxide in ethyl alcohol to an aqueous solution of ferrous sulphate, which has been saturated with the same gas; it separates in brown, glistening, small, rectangular plates, and slowly decomposes when exposed to the air.

The green and red compounds which are formed in concentrated hydrochloric acid, sulphuric acid, and organic solvents are to be regarded as additive products of ferrous sulphate or chloride with nitric oxide, having the formulæ $FeSO_4,NO$ and $FeCl_2,NO$, which in solution are possibly combined also with the solvent.

The results of this investigation throw light on the nature of the well-known "ring-test" for nitric acid; the colour of the "ring" will be either brown or red, according to whether the additive compound of ferrous sulphate and nitric oxide is formed in the concentrated sulphuric acid or aqueous layer. The reason why the coloration appears only at the boundary of the two liquids, although the nitrate has been dissolved, possibly in the ferrous sulphate solution, is due to the fact that the reduction of nitric acid proceeds much faster in concentrated sulphuric acid than in dilute acid solution. W. H. G.

Compounds of Nitric Oxide with Iron and Blood-Pigment. WILHELM MANCHOT (*Annalen*, 1910, **372**, 179—186).—A solution of ferric sulphate in 90% sulphuric acid at a temperature below 11° absorbs nitric oxide to the extent of 2 molecules of nitric oxide for each atom of iron, forming an intense deep red solution which probably contains the complex *salt*, $Fe_2(SO_4)_3,4NO$, combined with sulphuric acid. The complex salt is very unstable, and could not be isolated in a pure state; the solution in sulphuric acid, when placed in a vacuum or treated with a current of hydrogen, deposits ferric sulphate, and at the same time becomes colourless.

A ferric salt dissolved in concentrated hydrochloric acid does not combine with nitric oxide, but solutions of ferric chloride in acetone, amyl alcohol, and ethyl alcohol absorb nitric oxide, although in these cases the ferric salt is partly reduced.

It has been shown in a recent communication that blood-pigment combines with nitric oxide in the proportion of 2 molecules of the gas for each atom of iron (compare this vol., ii, 137); there can be little doubt, therefore, that the iron in hæmoglobin is present in the ferric state, for ferrous salts do not combine with more than one molecule of nitric oxide per atom of iron (compare preceding abstract). W. H. G.

Action of Coke on Solutions of Ferric Chloride. ALFRED TINGLE (*J. Amer. Chem. Soc.*, 1910, **32**, 540—541).—In an earlier paper (Abstr., 1909, ii, 405) the author has stated that the removal of iron from a ferric chloride solution by filtration through coke is probably due to the sulphur compounds present in the coke. Experiments have now been made which show that coke which has been carefully freed from sulphides does not withdraw any of the iron from a solution of ferric chloride, although part of the iron is reduced to the ferrous state. Under similar conditions, the coke does not have any effect on cupric chloride solutions. E. G.

Metallic Silicates. III. The Reaction between Solutions of Sodium Silicate and Ferric Chloride. EDUARD JORDIS and PAUL LINCKE (*J. pr. Chem.*, 1910, [ii], **81**, 289—313).—If a solution of ferric chloride is kept for a week at about 60°, and the precipitate filtered off, the filtrate is a stable solution, and can be reproduced. It is necessary to add sufficient hydrochloric acid to make the ratio Fe : Cl = 1 : 3. Sodium silicate solutions require the addition of

sodium hydroxide to make the ratio Na : $SiO_2 = 2 : 1$. The quantities of the solutions to be mixed are weighed and not measured.

For analysis, the evaporation should not be carried to complete dryness in the separation of silica; there is then no loss of ferric chloride at temperatures a little above 100°. The ferric hydroxide, precipitated from a hot solution, may be washed free from chlorine by means of dilute ammonia. The sodium is estimated as chloride by evaporation of the filtrate to dryness, and chlorine by distillation with sulphuric acid in a special apparatus.

If equivalent quantities of the two solutions are mixed, the precipitate contains all four components. The filtrate is practically neutral, but requires a considerable quantity of alkali to render it alkaline. A second precipitate is thus obtained, which contains less sodium and iron, but more chlorine, than the first. The composition varies with the time, and appears to lead to an equilibrium, the precipitate always containing sodium and chlorine in a complex condition. If the silicate solution is slowly added to the ferric chloride, no precipitate is produced until one-half of the equivalent quantity has been added. Iron must be present in such cases in a complex anion. Experiments showing the influence of time on the reaction are given. The precipitated gel is shown to differ chemically from the hydrosol previously present in the solution. C. H. D.

New Series of Solid Ammino-salts. G. Poma (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 223—228).—The gradual addition, with shaking, of 15 c.c. of 20% nickel sulphate solution to 50 c.c. of concentrated aqueous ammonia saturated with potassium iodide (bromide or chloride) results in the formation of a violet precipitate of microscopic crystals having the composition : $Ni(NH_3)_6SO_4,2KX$, where X = I, Br, or Cl. These salts are hygroscopic, and tend to lose ammonia and absorb water in its place, the colour changing from violet to green.

The following salts have been prepared by a similar method: $Co(NH_3)_6SO_4,2KI$ (or Br); $Cu(NH_3)_6SO_4,2KI$, an intensely blue, unstable precipitate; $Ni(NH_3)_6(ClO_3)_2,2KCl$ (or Br or I), violet, crystalline precipitates; $Co(NH_3)_6(ClO_3)_2,2KI$ (or Br). Attempts to prepare similar compounds from nickel nitrate or chloride resulted in the formation of simple ammino-compounds of the type $Ni(NH_3)_6X_2$.

This method affords a more rapid and convenient means of preparing known ammino-compounds than the methods usually employed. T. H. P.

Thorium Selenate. Grégoire Wyrouboff (*Zeitsch. Kryst. Min.*, 1910, **47**, 371—372).—The crystals of thorium selenate described by Rosati (Abstr., 1907, ii, 359) were stated to contain only $8H_2O$, although they are isomorphous with thorium sulphate and uranium sulphate with $9H_2O$. A new analysis proves that these crystals really contain $9H_2O$ (23·82%), as, indeed, was long ago determined by Cleve. L. J. S.

Mineralogical Chemistry.

Enargite and Covellite from Ouray Co., Colorado. WILLIAM M. THORNTON, jun. (*Amer. J. Sci.*, 1910, [iv], **29**, 358—359).—A sample of copper ore from the Genesse Vanderbilt mine in the Red Mountain district consisted of columnar enargite (anal. I, Cu_3AsS_4), indigo-blue covellite (anal. II, CuS), iron-pyrites, and quartz.

	Cu.	Zn.	Fe.	As.	S.	Total.
I.	50·82	0·33	trace	17·28	32·53	100·96
II.	68·38	—	—	—	32·51	100·89

L. J. S.

Phillipsite from Sirgwitz, Silesia. PHILIPPE BARBIER and FERDINAND GONNARD (*Bull. Soc. franç. Min.*, 1910, **33**, 79—81).—The large, twinned crystals of phillipsite found in cavities in basalt at Sirgwitz, near Löwenberg, although described crystallographically on several occasions, have not hitherto been analysed. The results now given agree with the formula: $15SiO_2,4Al_2O_3,5(Ca,Mg,K_2)O,20H_2O$. The presence of so much magnesium is noteworthy.

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	Loss on ignition.	Total.
45·21	21·34	6·41	4·53	3·49	18·86	99·84

L. J. S.

Beryl and Muscovite from Biauchaud (Puy-de-Dôme). PHILIPPE BARBIER and FERDINAND GONNARD (*Bull. Soc. franç. Min*, 1910, **33**, 74—78).—A pegmatite occurring near Biauchaud and near Cibertasse, in the canton of Olliergues, consists of quartz, microcline, muscovite, tourmaline, and beryl. The beryl is somewhat kaolinised; it gave anal. I, agreeing with the formula $H_2Gl_5Al_4Si_{11}O_{34}$. The muscovite gave anal. II., agreeing with

$$H_6(K_2,Na_2,Fe,Mg)_2Al_8Si_9O_{35}:$$

	SiO_2	Al_2O_3.	Fe_2O_3.	GlO.	MgO.	K_2O.	Na_2O.	Li_2O.	Loss on ignition.	Total.
I.	65·87	19·61	—	12·41	—	—	—	—	2·12	100·01
II.	46·42	34·85	1·95	—	0·27	10·03	1·31	trace	5·09	99·92

L. J. S.

Beryl from Montjeu (Saône-et-Loire). PHILIPPE BARBIER and FERDINAND GONNARD (*Bull. Soc. franç. Min.*, 1910, **33**, 78—79).—Beryl embedded in quartz occurs with tourmaline in a pegmatite at Montjeu. The following analyses agree with the formula

$$H_2Gl_5Al_4Si_{11}O_{34},$$

as for the beryl from Biauchaud (preceding abstract):

SiO_2.	Al_2O_3.	GlO.	Loss on ignition.	Total.
65·83	19·27	13·22	1·57	99·89
65·86	19·52	12·87	1·58	99·83

L. J. S.

Analyses of Some French Felspars. PHILIPPE BARBIER and FERDINAND GONNARD (*Bull. Soc. franç. Min.*, 1910, **33**, 81—86.)—I, from granite at Villeneuve, Côte-d'Or: traces of copper and of titanic acid are present in some specimens. The fact that this felspar contains a trace of lithium is considered to be sufficient proof that it is orthoclase rather than microcline (Abstr., 1908, ii, 704). II, from pegmatite at Chausseroze, Côte-d'Or: this also contains a trace of lithium, and is consequently regarded as orthoclase. III, from granite-porphyroid at Limonest, Rhône. IV, from Francheville-le-Haut, Rhône. V, from enclosures in basalt at Puy-de-Montaudan, near Royat, Puy-de-Dôme: the large crystals of orthoclase present in these enclosures are associated with crystals of oligoclase, zircon, calcite, ankerite, and zeolites: under V are given the results after deducting 4·28 and 4·38% CaO and the corresponding amount of carbon dioxide, due to the presence of admixed calcite.

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Li_2O.	Rb_2O.	Loss on ignition.	Total.
I.	65·87	19·38	0·38*	1·26	12·89	trace	—	—	99·78
II.	66·91	18·52	0·51	8·16	5·29	trace	—	0·39	99·78
III.	65·46	19·09	0·62	2·58	11·69	trace	nil	0·45	99·89
IV.	64·74	19·58	0·77	2·08	12·13	trace	trace	0·62	99·92†
V.	66·42	19·63	—	4·20	8·95	—	—	0·73	99·93
	66·31	20·41	—	3·71	8·72	—	—	0·83	99·98

* Including SrO. † Also trace Fe_2O_3.

L. J. S.

Secondary Felspar in Non-metamorphosed Sedimentary Rocks. F. GRANDJEAN (*Bull. Soc. franç. Min.*, 1910, **33**, 92—97).—Minute crystals of felspar, measuring 10—30 μ, are present in the chalk and in limestones of various geological periods (Carboniferous, Trias, etc.). The residue (about 0·01%) obtained by dissolving these rocks in hydrochloric acid consists mainly of felspar, together with zircon, etc. Determination of alkalis in this residue, as well as the optical characters, indicate that the felspar belongs to the microcline-anorthoclase series, with potassium predominating over sodium and with very little calcium.

L. J. S.

The Different Modes of Weathering of Silicates in the Earth's Crust. JAKOB M. VAN BEMMELEN (*Zeitsch. anorg. Chem.*, 1910, **66**, 322—357).—The product of the ordinary weathering of silicate rocks is clay, which consists of a mixture of mechanically disintegrated but chemically unchanged crystals of silicates, with a colloidal product of chemical alteration. Analyses of the latter portion, from nine different clays, show that it contains (1) a fusible silicate A, containing 2·9—6 mols. SiO_2 to 1 mol. Al_2O_3 in heavy clays and 3—5 mols. in light clays, and (2) a silicate B, resembling kaolin, containing 2—2·7 mols. SiO_2 to 1 mol. Al_2O_3. Crystalline kaolinite is not observed in ordinary clays. Volcanic clays are rich in A, the older clays contain increasing quantities of B. Kaolinite, zeolites, and other minerals are formed by the prolonged action of high temperatures or of heated water on clays.

In lateritic weathering the silica ratio falls below 3:1, and the

product contains aluminium hydroxide. Laterite is found in temperate climates as well as in the tropics, and in association with acid as well as with basic rocks. Lateritic and ordinary weathering sometimes proceed simultaneously. None of the hypothe-es yet proposed to explain the formation of laterite are tenable.

In pneumatolytic weathering, kaolinite, $Al_2O_3,2SiO_2,2H_2O$, is the product. True kaolin is to be distinguished from the product of ordinary weathering, which sometimes resembles it clo-ely. The absence of apatite and muscovite points to the formation of kaolin, as these minerals are very resistant to ordinary weathering, but readily decomposed by the pneumatolytic agent. The formation of "nests" of kaolin is discussed.

C. H. D.

A New Pennsylvania Meteorite. OLIVER C. FARRINGTON (*Amer. J. Sci.*, 1910, [iv], **29**, 350—352).—This meteoric iron was found while ploughing in 1907 about seven miles north of Shrewsbury in York County. The main mass weighed 24 lbs., and fragments found in the neighbourhood weighed 3 lbs. more. It is much weathered on the exterior. The structure is that of an octahedrite of medium coarseness, with broad bands of kamacite bordered by taenite; troilite nodules and schreifersite in hieroglyphic forms are also present. Analysis by Dickman and Mackenzie gave:

Fe.	Ni.	Co.	S.	P.	Total.
90·84	8·80	trace	0·01	0·29	99 94

L. J. S.

Physiological Chemistry.

The Influence of Alterations in Chemical and Physical Surroundings on the Blood-cells of Limulus, and Especially on their Granules. LEO LOEB (*Pflüger's Archiv*, 1910, **131**, 465—508).—Contact with raw surfaces does not affect pseudopodial formation, but causes solution of the granules; this may be due to metabolic changes, or else the permeability of the cell membrane is altered by the mechanical stimulus. The action of neutral salts is the sum of the action of their cations and anions. In a series of alkali salts with the anion constant, sodium occupies one, and ammonium the other end. Sodium salts further formation of pseudopodia, and the solution of the granules; ammonium salts act in the reverse way. The effects of numerous substances, including non-electrolytes, are described in full detail, and are interpreted in the language of ions and colloidal substances. The coagulation of limulus blood is believed to be a cell agglutination. W. D. H.

Further Investigations on the Substitution of Chlorine by Bromine in the Animal Organism, with a Contribution to the Subject of the Permeability of the Blood-Corpuscles. M. BÖNNIGER (*Chem. Zentr.*, 1910, i, 458; from *Zeitsch. expt. Path. Ther.*, 1909, 7, 556—560).—In continuation of animal experiments, the author shows that, also, *in vitro* the walls of the blood-corpuscles are permeable to Cl and Br ions, whereby the concentration of ions equivalent to that found in the serum is reached. If the serum is replaced by an isotonic sodium bromide solution, the chlorine of the corpuscles is almost completely displaced. Again, the bromine can be replaced by chlorine by placing the corpuscles back into a sodium chloride solution. The total halogen content of the corpuscles remains constant, and is hardly altered when they are placed in bromide solution; it is equivalent, in sodium chloride value, to about 0·27%. The author believes that bromides are not utilised physiologically, because they occur in at most small traces in food-stuffs. S. B. S.

The Biology of the Phagocytes. V. Action of Hypo-, Iso-, and Hyper-tonic Solutions of Halide Salts. HARTOG J. HAMBURGER and J. DE HAAN (*Biochem. Zeitsch.*, 1910, 24, 304—318).—The authors have investigated the action of hypo-, iso-, and hyper-tonic solutions of sodium chloride, bromide, and iodide on the phagocytic activity of leucocytes, using the method already described of counting the number of the cells which have ingested charcoal particles from a leucocyte-charcoal emulsion. Both hypo- and hyper-tonic solutions decrease the phagocytic activity, for which fact two factors are responsible, namely, (*a*) change in the water-content of the phagocytes, and (*b*) modification of the salt-content, through change of ions. In a foreign salt some of the native salts of the leucocytes diffuse out, and are replaced by foreign salts: for example, sodium chloride is replaced by sodium bromide. The amount of change is influenced by (*a*) the nature of the foreign salt, and (*b*) the amount of interchange. Iodides are more toxic than bromides. The more the composition of the solution deviates from an isotonic solution, the greater the interchange of ions and the stronger the suppression of phagocytic activity. The results confirm the view already expressed that the cell walls are permeable to anions. S. B. S.

The Biology of Phagocytes. VI. Action of the Salts of the Alkaline Earths on Phagocytosis. HARTOG J. HAMBURGER and J. DE HAAN (*Biochem. Zeitsch.*, 1910, 24, 470—477).—In contradistinction to calcium, neither barium nor strontium can increase the normal phagocytic power, nor restore the same if lost. Magnesium differs in its action from barium and strontium only in so far, that if the phagocytes have partially lost their phagocytic power by immersion in salt solution (for example, 0·9% sodium chloride), it can be restored by the addition of traces of magnesium salt. Magnesium is a normal constituent, therefore, of the phagocytes. Calcium has some specific action on the phagocytes, apart from its action as a bivalent element. S. B. S.

A Respiration Apparatus. Metabolism in Protracted Inanition. E. GRAFE (*Zeitsch. physiol. Chem.*, 1910, **65**, 1—20, 21—52).—An apparatus is described suitable for clinical work, which combines accuracy with a greater simplicity than is found in the more elaborate forms of apparatus.

Observations are recorded in a case of a girl in deep stupor, who took no food for about three weeks. Daily details of urine, etc., are given. The respiratory quotient sank to 0·69 ; a low quotient has been previously noted in professional fasters ; it points to the fact that fat is the principal substance burnt. Whether there is an increase of glycogen formation from protein is left uncertain. A subnormal quotient is not seen in acute infectious diseases in which very little nutriment is taken. The present patient exhibited the signs of acidosis. W. D. H.

The Laws of Digestion and Absorption. I. Methods. E. S. LONDON. **II. The Digestion of Finely-divided Meat in the Stomach.** E. S. LONDON and A. G. RABINOWITSCH. **III. The Quantity Relationships of the Digestive Juices.** E. S. LONDON and N. DOBROWOLSKAJA. **IV. The Secretion of Gastric Juice.** E. S. LONDON and A. J. SAGELMANN. **V. The Course of Gastric Digestion on a Mixed Diet, and the Origin of Constant Numbers.** E. S. LONDON and F. RIVOSCH-SANDBERG (*Zeitsch. physiol. Chem.*, 1910, **65**, 189—192, 193—195, 196—202, 203—206, 207—212). —I. The experiments designed for the elucidation of the laws discovered by the author and by Arrhenius were performed on polyfistulous dogs.

II. The square-root rule holds for the time occupied by the digestion of meat in the stomach.

III. The same law holds for the amounts of gastric and duodenal juice which are secreted.

IV. The same is true for the secretion of the "small stomach" in Pawloff's sense of the term.

V. A further mathematical discussion of the figures obtained on a mixed diet. In some cases a cubic root law holds good. W. D. H

The Chemistry of Digestion and Absorption in the Animal Body. XXXIX. Digestion and Absorption after Intestinal Resection. E. S. LONDON and W. DMITRIEW (*Zeitsch. physiol. Chem.*, 1910, **65**, 213—218).—Resection of the whole small intestine is fatal in about five weeks. Seven-eighths can, however, be resected in dogs. Metabolism of nitrogen and carbohydrates returns rapidly to the normal, but in relation to fats this is not the case. W. D. H.

London's Polyfistula Method. W. W. SAWITSCH (*Zeitsch. physiol. Chem.*, 1910, **65**, 280—282).—Polemical. The author objects to London's methods being described as new, seeing that they have been in use for the last eighteen years. W. D. H.

Gastric Lipase. I. Gastric Lipase in Human Embryo and New-born Child. JUSSUF IBRAHIM and T. KOPEĆ (*Zeitsch. Biol.*, 1909, **53**, 201—217).—Gastric lipase appears in the sixth month of

fœtal life, and after that date is present in the mucous membrane and contents of the stomach. It is not a mere back-flow of pancreatic juice. Addition of toluene destroys the activity of the enzyme.

W. D. H.

The Action of Thermal Influences on the Digestive Power of Gastric and Pancreatic Juices. H. ROEDER (*Biochem. Zeitsch.*, 1910, 24, 496—520).—The digestive power of pepsin and trypsin, in experiments where rapid digestion is carried out (the digestive power being determined by the Fuld edestin method), increases with increase of temperature, reaching its optimum between 50° and 55°. If, however, the ferments are warmed before being added to the digestion mixture, their activity is lessened. Warming for a few minutes even between 40° and 42° appreciably diminishes the digestive power both of pepsin and trypsin. The trypsin is more sensitive to thermal influences than the pepsin. Low temperatures (even that of liquid air) do not appreciably affect the activity. Most of the experiments were carried out with digestive juices from a dog; experiments with human digestive juices from a child with a fistula gave similar results.

S. B. S.

The Influence on Nitrogenous Metabolism of Rabbits of Nucleic and Uric Acids and Allantoin. Formation of Nucleic-Uric Acid Compounds. ALFRED SCHITTENHELM AND PHILIPP SEISSER (*Chem. Zentr.*, 1910, i, 36—37; from *Zeitsch. expt. Path. Ther.*, 1909, 7, 116—133).—The authors investigated the influence of the addition of sodium nucleate alone, and sodium nucleate and uric acid together, to the fodder of rabbits, the observations lasting over four weeks. Almost all the purine products excreted were in the allantoin fraction of the urine. No more complete uric acid excretion or diminished uric acid destruction could be determined when nucleic acid was given at the same time. Intravenous injection of nucleic acid caused an increase only in the purine bases and allantoin. Ingestion of allantoin caused a marked increase in the total nitrogen excreted; and the allantoin excreted was nearly double that ingested. S. B. S.

Ferment Concentration in Pure Pancreatic Juice. D. HIRATA (*Biochem Zeitsch.*, 1910, 24, 443—452).—The experiments were carried out on a dog with pancreatic fistula. The amounts of juice secreted in ten minutes intervals were determined, and the amount of diastase contained therein was estimated by Wohlgemuth's method. Sodium hydrogen carbonate, calcium carbonate, and pilocarpine caused the secretion of small amounts of juice with a high ferment concentration; hydrochloric acid and aluminium acetate caused secretion of large amounts of juice with low ferment concentration; tannic acid, magnesia usta, gentian, and saline caused small secretion of low concentration. S. B. S.

The Relationship between the Total Nitrogenous Metabolism and the Uric Acid Excretion. H. BIERNACKI (*Chem. Zentr.*, 1909, i, 41; from *Zeitsch. expt. Path. Ther.*, 1909, 7, 134—153).—From

experiments on dogs, the author draws the conclusion that the addition of fats and carbohydrates to food-stuffs decreases both the total nitrogenous metabolism and the uric acid output. The output of purine bases, on the other hand, increases. The relationship of these facts to the theory and therapy of gout is discussed. S. B. S.

Investigations of Protein Metabolism in Children. PAUL GROSSER (*Biochem. Zeitsch.*, 1910, **24**, 346—353).—The influence of the amount of water ingested on the nitrogen excreted in urine and fæces was investigated. In the case of an alcaptonuric child, the ratio of total nitrogen to homogentisic acid was investigated at the same time. The author concludes that water has but little influence on the nitrogen excretion, provided that the experiment has extended over a sufficiently long period. S. B. S.

Effect of Non-protein Nitrogen Compounds on the Protein Metabolism in Ruminants. OSKAR KELLNER, P. EISENKOLBE, R. FLEBBE, and R. NEUMANN (*Landw. Versuchs.-Stat.*, 1910, **72**, 437—458).—The results of feeding experiments in which lambs were supplied with nitrogen almost exclusively in the forms of asparagine and ammonium acetate showed that these substances, as changed by the micro-organisms in the mixed food, can take the place of the protein necessary to maintain the animals. Both substances, added to food containing protein, may bring about an increase in the deposition of nitrogen. In this case they take the place of the protein required for maintenance, and thus render a portion of the protein of the food available for flesh production. With foods deficient in protein, no production of flesh from asparagine and ammonium acetate could be obtained, even with growing animals. N. H. J. M.

Sodium Chloride Metabolism and Sodium Chloride Action in Healthy Men. R. TUTEUR (*Zeitsch. Biol.*, 1910, **53**, 361—385).—An absolute daily sodium chloride equilibrium is never obtained in healthy men, whether the salt be given in small, medium, or large doses. Retention usually occurs. The salt given is, however, usually excreted within forty-eight hours. The amount in the fæces is very small unless the dose is very great. The excretion of water and of chlorine by the kidneys runs parallel. With small doses of salt, the fæces are relatively rich in water. Moderate doses of salt act beneficially in the maintenance of nitrogenous equilibrium. W. D. H.

Physiology and Pathology of Sodium Chloride Metabolism. HEINRICH VON HOESSLIN (*Zeitsch. Biol.*, 1909, **53**, 25—92).—After the constant administration of large amounts of sodium chloride, the salt is all excreted by the kidney; the excretion exhibits, however, a periodicity which is not entirely parallel to the intake of water. After a single large dose, it is all excreted in the twenty-four hours; if retention occurs, it is due either to poorness of the body in salt, or to insufficiency of kidney action, and this is accompanied by retention of water. Salt has a "sparing" action on protein catabolism, and causes an increased excretion of phosphates. Large quantities of water have a favourable

effect on protein metabolism. Elevation of the body-temperature leads to a retention of sodium chloride, apparently without injuring the kidney functions. This is not due to water retention alone. In alterations of the circulation by atropine, carbon monoxide, or bleeding, retention also occurs, and the retention in infectious diseases is mainly due to insufficiency of heart action rather than of kidney action.

W. D. H.

Oxalic Acid Metabolism. ZDZISLAUS TOMASZEWSKI (*Chem. Zentr.*, 1910, i, 41; from *Zeitsch. expt. Path. Ther.*, 1909, **7**, 215—224).—The author added to pastes of various organs (kidney, spleen, liver, and blood) sodium oxalate and alkaline solutions of uric acid, and then estimated the uric acid (by the Krüger-Schmidt method) and oxalic acid (by the Autenrieth-Barth method) after incubation at 37°. He found that a part of the uric acid is oxidised to oxalic acid, and this newly-formed oxalic acid can be further decomposed, especially in the kidneys.

S. B. S.

The Difference in Nutritive Value of Proteins in Relation to their Composition. I. JOSEF ZISTERER. **II.** ERWIN VOIT and J. ZISTERER (*Zeitsch. Biol.*, 1909–10, **53**, 157—200, 457—498).—Metabolic experiments with muscle-protein, casein, and aleuronate show that their nutritive value may be expressed by the figures 100, 112, and 110 respectively. This is no doubt related to differences in their composition, but the figures show that the nutritive difference is of little practical importance.

A comparison of the nutritive value of casein with that of its cleavage products shows that the latter is the smaller; the conclusion is drawn that complete cleavage does not occur in the alimentary tract, and the higher value of the intact protein is due to certain compounds of the final products being absorbed as such.

W. D. H.

The Synthesis and Cleavage of Proteins in the Animal Organism. EMIL ABDERHALDEN and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1910, **65**, 251—255).—The view that amino-acids are absorbed as such and pass into the circulating blood is not supported by analyses of the blood. This may be due to the methods used not being sufficiently delicate to detect small quantities of amino-acids. Another view is that protein is resynthesised in the wall of the alimentary canal, but no support to this view was obtained in the present research. No differences in the yield of protein and its cleavage products could be detected in the wall of the intestine after the administration of protein or amino-acids as compared with the fasting state.

W. D. H

The Influence of the Salts in Drinking Water on Physical Development. RAGNAR BERG [and, in part, CARL RÖSE] (*Biochem. Zeitsch.*, 1910, **24**, 282—303).—The author summarises and amplifies the observations of Röse, which tend to show that the harder the drinking water of a district, the better the physical development of the children. The conclusions are drawn chiefly from examination

of the teeth of children from different districts of which the hardness of the water is known, and by comparing the number of recruits capable of military service from similar districts. Detailed examination has also been made of the composition of the saliva under the influence of drinking water of varying hardnesses, and of diets containing varying quantities of calcium. The amount of saliva excreted increases with the hardness of the drinking water, and in neighbourhoods with hard drinking water, the children secrete a saliva which is both relatively and absolutely more alkaline than that secreted by children reared in neighbourhoods with soft drinking water. Detailed analyses of the bases and acids of the saliva indicate that the increased alkalinity is due to organic bases. The amount of mucin in the saliva runs also fairly parallel with the alkalinity. A preliminary summary is also given of the influence of calcium salts on the quantity and character of other secretions. S. B. S.

The Content in the Human Organs of Chlorine, Calcium, Magnesium, Iron, Water, Protein, and Fat. ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1910, **24**, 363—380).—The analyses were carried out with the organs of a healthy man which seemed to be completely normal. The details of the analytical methods are given, and the results obtained are stated in lengthy tables, in which are incorporated, for comparison, those given by other investigators for healthy organs of human beings and animals. S. B. S.

The Properties and Modes of Action of the Diastatic Ferment in Warm-blooded Animals. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, **24**, 191—209).—The amount of diastase in an organ can be best estimated by obtaining the tissue in the form of powder by Wiechowski's method. The powder is then emulsified with water, starch solution is added, and the concentration of the enzyme in the emulsion determined by Wohlgemuth's method. The mixture must be kept shaken, however, during the whole of the incubation period, as the tissue proteins coagulate and adsorb the ferment. It was found, in contradistinction to earlier observers, that the amount of diastase in the liver does not diminish during the first twenty-four hours after death. The previous erroneous results were due to the fact that the coagulum formed adsorbed the ferment; the error due to this fact is avoided by shaking during incubation. Within certain limits, the action of the diastase is not influenced by its concentration. The amount of action is, however, influenced by the concentration of the substrate, whether the latter be glycogen or starch. The liver diastase goes quantitatively into the plasma of the organ. A more powerful diastase can be prepared by precipitating the latter by alcohol than can be obtained from the original plasma. This is due to the fact that the alcohol removes certain substances which inhibit the ferment action. The ferment is not used up during its action, but can act on successively added quantities of substrate. The diastatic capacity of the livers of rabbits is very variable. With rabbits of the same size, the diastatic action is greater in those animals which have been killed by bleeding than in those killed by

breaking the neck. This is probably due to the removal by bleeding of certain inhibitory substances. An increase of diastase was not observed either after piqûre or adrenaline injection. Ingestion of glycerol causes a washing out of ferment from the organ, and an increased excretion of diastase in the urine can be observed as a consequence. This fact explains the inhibitory action of glycerol on the effect of piqûre and adrenaline ingestion. S. B. S.

Normal Secretion by the Liver of an Anticoagulating Substance. MAURICE DOYON (*Compt. rend.*, 1910, **150**, 792—793).—An antithrombin is produced when arterial blood is circulated through the isolated liver of a dog. Under these conditions, the blood does not coagulate, and it inhibits the coagulation of normal blood *in vitro.* Blood withdrawn from the subhepatic veins coagulates only after several hours. These observations appear to show that fibrin does not necessarily undergo destruction in the liver, but that fibrinogen has an hepatic origin, an hypothesis that is supported by the fact that the latter substance is absent from the plasma when the liver is excised or affected by serious lesions. W. O. W.

Uric Acid Formation. VI. GUIDO IZAR (*Zeitsch. physiol. Chem.*, 1910, **65**, 78—88).—The reappearance of uric acid after its destruction, noted in previous researches, depends on the co-operation of an enzyme which is present in the blood and a co-enzyme which is furnished by the liver and spleen, but which is absent in the kidney. The co-enzyme is thermostabile and soluble in alcohol. W. D. H.

The Influence of Bile on Fat Synthesis due to Intestinal and Pancreatic Lipase. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1910, **65**, 232—245).—The addition of bile accelerates the synthesis of fat which is brought about by lipase; this is due to the bile salts and bile alkalis. W. D. H.

The Pancreas of the Elephant. ENRIQUE FERNANDEZ (*Chem. Zeit.*, 1910, **34**, 331).—The alcoholic extract of the pancreas of an elephant was precipitated with ether, and yielded 5% of pancreas ferment. In six days, fat was hydrolysed by the ferment to the extent of 65%; neutralisation accelerated the action. At 15°, 0·0004 gram of the ferment liquefied 0·25 gram of starch in five minutes; in fifteen minutes, 0·2 gram of starch was fully converted into dextrin and dextrose by 0·00025 gram of the ferment.

Sucrose was but slightly affected, and maltose remained unchanged. White of egg was rapidly peptonised at 40°. L. DE K.

The Presence of Iodine in the Human Pituitary. H. GIDEON WELLS (*J. Biol. Chem.*, 1910, **7**, 259—262).—Iodine cannot be regarded as a normal constituent of the pituitary gland. When present, as it sometimes is, in traces, it is probably due to previous drug treatment with iodides. This was confirmed by experiment.

W. D. H.

The Possible Vicarious Relationship between the Pituitary and Thyroid Glands. SUTHERLAND SIMPSON and ANDREW HUNTER (*Quart. J. expt. Physiol.*, 1910, 3, 121—128).—The normal pituitary (ox and sheep) contains no iodine; the same is true for the pituitary after thyroidectomy. If it is accepted that the iodine-containing substance represents the active principle of the thyroid, these experiments yield no support to the view of a vicarious relationship between that organ and the pituitary. W. D. H.

Factors Influencing the Processes of Diffusion through the Fresh Intestinal Membrane of Animals. ERNST MAYERHOFER and ERNST PŘIBRAM (*Biochem. Zeitsch.*, 1910, 24, 453—469).—The experiments were carried out by determining the rate of diffusion of potassium chloride through pieces of the small intestine, comparing the rates when the latter had been altered in different ways. The rates of diffusion through similar pieces of intestine of normal animals, and those of animals in pathological condition were also investigated. It was found that the permeability was a function of the water-content of the intestine. Intestines subjected to artificial imbibition of water (corresponding with intestines in cases of acute enteritis) had an increased permeability; those, on the other hand, which had been partly dried (corresponding with the condition of intestines in chronic enteritis) had diminished permeability. The more capable of imbibition the membrane is, the more readily it can be converted from one state to another. When a tissue has once lost its power of imbibition in the organism (chronic enteritis), the permeability can only be altered with difficulty by artificial means outside the organism. S. B. S.

The Formation of Creatine in the Muscles at the Tonus and in the Development of Rigidity. C. J. C. VAN HOOGENHUYZE (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 550—562).—The creatine was estimated by heating the tissues with 0·1% hydrochloric acid for half an hour at 110°, separating the protein, and then estimating the creatinine colorimetrically by Folin's method. The results indicate the production of creatine when the muscles are in a long-continued state of tonus, as opposed to rapid contraction produced by electrical stimulus. In the latter case the author and other observers have generally failed to notice increased production of creatine. The author has, however, observed increased production in the case of tonus. This was produced in cats by decerebration. The posterior roots were cut on one side, and left intact on the other. On the side on which the posterior roots were intact, decerebrate rigidity was produced, and an increase of creatine could be detected in the leg muscles, when compared with the other side, when the tonus was absent. Similar results were obtained in the case of frogs, where the absence of tonus was produced by section of the sciatic nerve. By periodic stimulation of the nerve, however, no certain increase of creatine could be obtained. Increase of creatine was also noticed when muscles were stimulated after the action of drugs which have a tonicising influence, such as veratrine, nicotine, and

calcium chloride, sodium thiocyanate, and caffeine citrate. This increase was only marked after excitation of the muscles. Increase of creatine was also observed in post-mortem rigidity. S. B. S.

The Lecithin Content in the Bone-marrow of Man and Domestic Animals. A. BOLLE (*Biochem. Zeitsch.*, 1910, **24**, 179—190).—The method generally employed was to make an alcoholic extract of the marrow at 60°, and then a chloroform extract of the residue obtained after evaporation of the alcohol. The phosphorus was estimated in the product thus obtained. It was found that the formation of the bone-marrow commences in the fœtus of pigs at the fourth month, and in that of oxen at the sixth month. With increasing age, fat takes the place of red blood-corpuscles. Lecithin is a constant constituent of this fat, and its amount increases with increasing age. In the case of paralysed individuals, a disappearance of, or impoverishment of, the bone-marrow in lecithin could be ascertained. The analyses confirm in the main the results of Glikin and Peritz. S. B. S.

Chemical Processes in the Earthworm. III. Anoxybiotic Decomposition of Glycogen. ERNST J. LESSER (*Zeitsch. Biol.*, 1910, **53**, 532—544. Compare Abstr., 1909, ii, 419).—The anoxybiotic decomposition of glycogen is about sixfold that which occurs oxybiotically. Glycogen is therefore the parent substance of the carbon dioxide and fatty acids which originate in the anoxybiotic state. These products, however, only account for about half of the glycogen which disappears; methane and hydrogen are not produced anoxybiotically. W. D. H.

Chemical Processes in the Earthworm. IV. Gaseous Metabolism in the State of Anoxybiosis. ERNST J. LESSER (*Zeitsch. Biol.*, 1910, **54**, 1—17. Compare preceding abstract).—The respiratory exchange was investigated with an apparatus constructed on the Regnault-Reiset principle. In anoxybiosis during the first nine days of inanition, the respiratory quotient of the earthworm rises above the normal; the fatty acid found cannot, therefore, be the chief substance which undergoes combustion in this condition.

W. D. H.

Secretion of Phromnia marginella. DAVID HOOPER (*J. Asiatic Soc. Bengal*, 1909, **5**, 363—366).—The white, manna-like incrustation deposited by the "ghost-bug" (*Phromnia marginella*) on the leaves of *Elaeodendron glaucum* is found to contain dulcitol.

T. A. H.

The Partition of Nitrogen in Human Milk. A. FREHN (*Zeitsch. physiol. Chem.*, 1910, **65**, 256—280).—The caseinogen nitrogen obtained by investigating the precipitate produced by acetic acid (Engel's method) varied in twenty-seven women between 30 and 53% of the total nitrogen, or in the mean 43%. The causes of variation are far from clear. The percentage of caseinogen is therefore 0·4 to

0·7. The paper discusses the possibilities of the various compounds, protein and otherwise, in which the remainder of the nitrogen is present. W. D. H.

The Purine Enzymes in the Rat. ALICE ROHDÉ and WALTER JONES (*J. Biol. Chem.*, 1910, **7**, 237—248).—Rats' urine contains uric acid, yet the extracts of the organs yield neither adenase or xanthooxydase. This may be due to the fact that extracts do not give a true picture of what occurs *in vitro*; or else this may, like the presence of hypoxanthine in dog's muscle, be an example of the origin of uric acid by processes which do not involve the action of the purine enzymes. The recent work of Ascoli and Izar gives colour to the second hypothesis.
W. D. H.

Excretion of Sodium Ferrocyanide by the Kidney in Dogs. NIKOLAI WASCHETKO (*Zeitsch. Biol.*, 1909, **53**, 128—133).—The place where sodium ferrocyanide is excreted is the specific renal epithelium; it can be detected in the cell protoplasm by the Prussian-blue reaction, also in the lumen of the tubules, in the blood vessels and lymph spaces of the adjacent connective tissue, and in the basement membrane of the tubules. In the lumen of Bowman's capsule, no precipitate is found under normal conditions; when it is present, it is due to accidental back flow.
W. D. H.

Urobilin Excretion. TSUCHIYA (*Chem. Zentr.*, 1910, **1**, 40; from *Zeitsch. expt. Path. Ther.*, 1909, **7**, 263—278).—Urobilin was estimated in the urine of dogs with a biliary fistula, and in women during the menstrual period. The excretion is small during starvation, and increases during menstruation, both in starvation and in normal individuals. The results indicate a parenteral origin of urobilin. The latter was estimated in a Martens spectrophotometer after the separation of the uric acid and hæmatoporphyrin by means of barium hydroxide and barium chloride solutions; from such solutions freed from uric acid and hæmatoporphyrin, it was precipitated by ammonium sulphate (after removing excess of barium), and dissolved in one part of ether and two parts of alcohol.
S. B. S.

Trypsinogen and Trypsin in Urine. E. GRAF VON SCHOENBORN (*Zeitsch. Biol.*, 1910, **53**, 386—428).—Trypsin occurs in urine seldom, and then only in minimal quantity; trypsinogen, however, is found in dog's urine, and can be activated by kinase; its amount is increased by a meat diet, and also in inanition; in the latter condition, trypsin may be present also. A substance is also present which resists boiling, and which increases the action of trypsin. In several pathological human urines, a strong antitryptic action can be demonstrated.
W. D. H.

Colloids in Urine. II. Relationship between Colloids and Solubility of Uric Acid and Urates. L. LICHTWITZ (*Zeitsch. physiol. Chem.*, 1910, **64**, 144—157. Compare Abstr., 1909, ii, 750; Menz, *ibid.*, i, 343).—Urine contains colloids of the type of gelatin

namely, colloids which are shown by the ultra-microscope to become more finely-divided with rise of temperature. The solubility of uric acid and urates in urine depends on (*a*) temperature, (*b*) concentration of hydrions (Henderson and Spiro, Abstr., 1909, ii, 165), (*c*) amount of colloids, and (*d*) state of division of the colloid. Under specific conditions, it can be shown that a quantitative relationship exists between the solubility of uric acid and the condition of the colloid. Urines which contain precipitated uric acid and urates become clear when boiled, but not when heated at 40—50°. In a few cases, the uric acid is precipitated again immediately the solution cools, and in such cases the protecting action of the urine on gold solutions is the same before and after boiling. In the majority of cases the precipitate of uric acid appears very slowly when the solution is cold. This is due to the fine state of division of the colloid produced by boiling, and it is found that in such cases the boiled urine has a much more pronounced protective action on gold solutions than unboiled urine.

In normal urine the whole of the uric acid is present in the form of a true solution. J. J. S.

Duodenal Diabetes. E. TSCHERNIACHOWSKI (*Zeitsch. Biol.*, 1909, 53, 1—11).—Pflüger believed that pancreatic diabetes was really of nervous origin, and stated that removal of the duodenum produced the same result. The present experiments on dogs do not confirm this view. There is, however, a temporary glycosuria, and this follows not only resection of the duodenum, but also of other parts of the small intestine, or division of the mesentery. W. D. H.

The Physiological Behaviour of Radium Emanations. ANNA LASKA (*Biochem. Zeitsch.*, 1910, 24, 357—362).—The emanations introduced into the blood-stream are rapidly eliminated in the expired air. Emanations introduced *per os* slowly and gradually diffuse into the blood, and also leave the organism in the expired air. During inhalation of emanations, the latter enter into the circulation as long as the inhalation is continued. The fæces show radioactivity only when the emanations are introduced in solid form. No particular affinity of the emanations for any particular organ could be detected. The results are arrived at as a result of experiments on the human subject and on animals. S. B. S.

The Action of Potassium Bromate. KARL G. SANTESSON (*Arch. Fisiol.*, 1909, 7, 541—556).—Certain commercial samples of potassium chlorate contain the bromate as an impurity. For this reason an investigation was made of the pharmacological action of the bromate. It was found to be two and a-half times more toxic than the chlorate when tested on frogs; both salts paralyse both the heart and the central nervous system. On the isolated frog's heart, the chlorate acts more powerfully than the bromate; the more intensive action of the latter on the whole animal is due therefore to the action on the central nervous system. Both salts dilate the heart, and diminish both the volume and frequency of the pulse. On rabbits the bromate

acts, also, more toxically than the chlorate. This is not due to the action on the blood, and scarcely any change can be noticed in it in the case of rabbits. The bromate produces, however, violent diarrhœa and wasting, and when injected intravenously in large doses it causes dyspnœa and convulsions. A mixture of 5—15% bromate with chlorate causes in the case of rabbits hardly any effect. The action of the catalase (peroxydase) of the frog's muscle on hydrogen peroxide is inhibited by both the chlorate and the bromate, the former salt having a more powerful action in this respect; acting noticeably even in a dilution of 0·00074% S. B. S.

Behaviour of Hypophosphites in the Organism. ALDO PATTA (*Arch. Farm. sper. Sci.*, 1909, **8**, reprint 10 pp.).—Phosphates and phosphites administered to an animal reappear in the urine as phosphates almost quantitatively. When sodium hypophosphite is injected, however, a varying portion of it is eliminated unchanged, but the amount of phosphate in the urine is not increased. With large doses (2 grams) one half escapes oxidation, whilst when smaller doses (0·6 gram) are employed, the proportion eliminated is about one-sixth. Twenty-four hours after the administration, no hypophosphite, or at most only a trace, is to be found in the urine.

The determination of the hypophosphite is effected as follows. The urine is acidified with acetic acid, and the phosphate precipitated with uranium acetate. One half of the filtered liquid is acidified with hydrochloric acid, treated with an excess of mercuric chloride, and the precipitate of mercurous chloride is weighed. The other half is oxidised with nitric acid, and determined as phosphate. R. V. S.

The Behaviour of Organic Arsenic Preparations in the Human Body. THEOPHILE FISCHER and J. HOPPE (*Chem. Zentr.*, 1910, i, 44; from *Münch. med. Woch.*, 1909, **56**, 1459—1461).—Atoxyl and arsacetin are eliminated in the urine more rapidly and completely than arsenophenylglycine; by repeated administration of the latter drug, the rate of arsenic elimination is diminished; it is also eliminated to a larger extent in the intestine than is the case with the two other drugs. The arsenic in this case goes more into the blood, and shows a marked avidity for the lecithin. S. B. S.

Physiological Behaviour of Iminoallantoin and of Uroxanic Acid. TADASU SAIKI (*J. Biol. Chem.*, 1910, **7**, 263—265).—When iminoallantoin (Denicke, Abstr., 1906, i, 938) is introduced parenterally into rabbits, toxic symptoms are not observed, and the purine contents of the urine do not increase; unaltered iminoallantoin is found in the urine, and a considerable increase in the amount of oxalic acid is noticeable.

When sodium uroxanate is used, somewhat similar results are observed. J. J. S.

Comparative Physiological Power of Chloroform, Alcohol, and Ether, Measured by their Effects on Arterial Blood-Pressure. AUGUSTUS D. WALLER and W. LEGGE SYMES (*Quart. J. expt. Physiol.*, 1910, **3**, 115—120).—The relative narcotic power of

these drugs, as judged by their effects on lowering blood-pressure, works out about the same as those indicated by previous experiments on frog's muscle (Abstr., 1909, ii, 75), namely, the molecule of chloroform is one hundred to one hundred and ten times as powerful as that of ethyl alcohol, and thirteen times as powerful as that of ether.

W. D. H.

Behaviour of Iodoso-, Iodoxy-, and Iodonium-compounds in the Animal Organism. I. Behaviour of Iodosobenzene. RICCARDO LUZZATTO and G. SATTA (*Arch. Farm. sper. Sci.*, 1909, 8, reprint 29 pp.).—From experiments with dogs and rabbits, the authors find that iodosobenzene is a fairly toxic substance, the fatal dose being 0·15—0·20 gram per kilo. of body-weight. The toxicity seems to be due to the substance itself, rather than to its probable decomposition product, iodobenzene. No iodosobenzene is eliminated unchanged, but the urine contains both organic and inorganic iodine. It is probable that iodophenylmercapturic acid is the iodine derivative present in greatest amount, and this would indicate that the substance is reduced in the organism to iodobenzene. In the case of a rabbit to which small quantities of iodosobenzene had been administered for eight days, the distribution of iodine was found to be as follows: thyroid gland, 0·39% (of fresh substance); blood serum, 0·05 gram per 100 c.c.; kidney, 0·244%; liver, 0·142%; lung, 0·070%; muscles, 0·058% (of dry substance in each case). Traces were found in the submaxillary gland, spleen, ovary, and blood coagulum. None was found in the peritoneal fat or in the brain, so that the substance (which is insoluble in lipoids) does not localise itself in the brain. The toxic effect is, however, due to action on the central nervous system. Experiments with frogs did not reveal any curare-like action.

R. V. S.

Degradation of Di-iodotyrosine in the Animal Organism. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1910, 65, 141—156. Compare Abstr., 1909, ii, 1041).—Di-iodotyrosine, when administered to rabbits, gives up 40—45% of the iodine in the inorganic form. About 7% remains unaltered, the balance being recovered in the form of an organic acid crystallising in needles, m. p. 75°, and soluble in alcohol and acetone; also a similar acid, m. p. 95°; further, a substance soluble in ether, which readily decomposes, and lastly, an acid, crystallising in colourless plates, which is unstable towards light, and possibly represents a phenolic compound containing iodine in the nucleus.

E. F. A.

The Action of Tetrahydro-β-naphthylamine on the Body-temperature and Circulation. G. P. SACHAROFF (*Chem. Zentr.*, 1910, 1, 42; from *Zeitsch. expt. Path. Ther.*, 1909, 7, 224—241).—When the animals (rabbits) are not bound down or under morphine, the drug causes a marked increase of temperature by direct stimulation of the heat centre, and a diminished loss of heat, due to spasms of the cutaneous vessels. The increase of arterial pressure is due to contraction of the peripheral vessels. S. B. S.

The Influence of Strophanthine, Adrenaline, and Muscarine on the Electro-cardiogram. H. STRAUB (*Zeitsch. Biol.*, 1909, **53**, 106—122).—The electro-cardiogram was obtained from the exposed hearts of narcotised cats and rabbits by the string-galvanometer, and the changes produced by the three drugs mentioned were registered. These are irregular and difficult to interpret. W. D. H.

The Physiological Action of Tartaric Acids. LÁSZLÓ KARCZAG (*Zeitsch. Biol.*, 1909, **53**, 218—231).—The four isomeric tartaric acids were examined by intravenous injection for their effect on the cardio-inhibitory and vaso-motor centres; they were also tested on the isolated cardiac auricle and ventricle. In the former case the *d*-acid is least, and the *l*-acid most active; the *r*- and *i*-acids are intermediate. On the isolated ventricle the *i*-acid is least active. W. D. H.

Action of Yohimbine on the Heart, with Special Reference to Toxic Heart-block. JOHN TAIT (*Quart. J. expt. Physiol.*, 1910, **3**, 185—208).—Yohimbine does not affect the A/S ratio, where A is the duration of the absolutely refractory phase, and S the time of systole. In sufficient concentration, it greatly prolongs the relatively refractory phase; it depresses the irritability of the tissue to stimulation, and it readily fatigues the conducting mechanism, but does not depress contractility. Irritability and conductivity are, as in nerve, essentially the same property, and toxic heart-block is due to a depressing action on the excito-conducting mechanism. W. D. H.

Toxicity of Elemental Arsenic. LECOQ (*Compt. rend.*, 1910, **150**, 887—888. Compare this vol., ii, 406).—Pure colloidal arsenic is much less toxic to animals than arsenious oxide. W. O. W.

Toxic Action of Isomeric Butyric and Hydroxybutyric Acids on Frog's Muscles and Nerves. LÁSZLÓ KARCZAG (*Zeitsch. Biol.*, 1909, **53**, 93—105).—On normal and curarised frog's muscle, the toxicity of butyric and *iso*butyric acids is about equal; α-hydroxybutyric acid is, however, more poisonous than α-hydroxy*iso*butyric acid, and this more so than β-hydroxybutyric acid. The position of the hydroxyl in the molecule also makes a difference, the toxicity diminishing the further the hydroxyl is from the carboxyl; this is illustrated by the relative activities of α- and β-hydroxybutyric acids. Increase in the number of hydroxyl groups increases the poisonous action; thus $\beta\gamma$-dihydroxybutyric acid is more poisonous than the β-hydroxy-acid.

On the muscle-nerve preparations, butyric and β-hydroxybutyric acids in one case, and the *iso*butyric and α-hydroxybutyric acids in another, act in the reverse way to that in which they act on muscle. The acids are more poisonous, and act more rapidly on the end-plates, than the hydroxy-acids; otherwise the results are parallel. W. D. H.

Tolylenediamine Poisoning. GEORG JOANNOVICS and ERNST P. PICK (*Chem. Zentr.*, 1910, i, 43; from *Zeitsch. expt. Path. Ther.*, 1909, **17**, 185—214).—Tolylenediamine does not act hæmolytically *in vitro*. It can be made to act *in vivo* either as an acute or chronic poison, acting in the latter case for several weeks. The methyl-alcoholic extract of the liver in acute cases furnishes a powerful hæmolysin, which, although not oleic acid (it having a lower iodine number), is allied to the fatty acids. In chronic cases of poisoning this hæmolysin is yielded only in small quantities, being apparently attached to the blood-corpuscles. In chronic cases of poisoning, the hæmolysis is accompanied by fatty degeneration of the liver. The time of onset and extent of the latter is inhibited by removal of the spleen. The authors give details of the method for the preparation of the hæmolysin.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Semi-Specific Chemical Disinfectants. HEINRICH BECHHOLD (*Zeitsch. Hyg. Infektionskrankheiten*, 1909, **64**, 113—142).—A detailed account of experiments on the germicidal power of a large number of compounds; their relative action in various concentrations, at different temperatures, and periods of time on commonly occurring pathogenic organisms in broth cultures. Tabulated results are given for the halogen derivatives of β-naphthol and naphtholsulphonic acids.

Tribromo-p-*di*-o-*cresol*, colourless aggregates, m. p. 162°, was prepared and compared with other similar compounds.

Tribromo-β-naphthol was found to exert its maximum germicidal power with *B. streptococcus*, *B. staphylococcus*, and the diphtheria bacillus, whilst dibromo-β-naphthol reacted similarly with *B. coli*. A bromine atom was found to impart greater germicidal power than did a similarly placed sulphonic group. F. M. G. M.

The Biological Absorption of Methane, and the Distribution of Kaserer and Sohngen's Organism in Soils, Manure, etc. ITALO GIGLIOLI and GIULIO MASONI (*Staz. sperim. agrar. ital.*, 1909, **42**, 589—608).—The authors confirm Kaserer and Söhngen's observations as to the presence of methane-destroying organisms, which action they state is of biological nature, and independent of ferments. Light has no influence on the absorption, the optimal temperature of which is about 30°, but which varies slightly with different organisms. The upper layers of the soil are poorer in the organisms than the lower layers. S. B. S.

Experiments on Ammonia and Nitrate Formation in Soils. JACOB G. LIPMAN and PERCY E. BROWN (*Centr. Bakt. Par.*, 1910, ii, **26**, 590—632).—Addition of dextrose to soil resulted in an

enormous increase in the number of bacteria present, whilst sodium citrate caused a still greater increase. Subsequently, there was a great reduction of the numbers of bacteria in all the soils; the numbers in the treated soils, however, remained in excess of the numbers in untreated soil.

Experiments in which sterilised soil containing peptone, dried blood, and cotton-seed meal respectively, both without and with dextrose, were innoculated with *B. mycoides* showed in every case considerable production of ammonia. Addition of dextrose to peptone decreased the amount of ammonia produced, whilst in the case of dried blood, ammonification was greatly increased by addition of dextrose. With cotton-seed meal, addition of dextrose had very little effect.

Ammonification and nitrification experiments are described, in which the various substances were mixed with soil (100 grams) and the ammonia and nitrates determined after six days and four weeks respectively. The substances employed were: (1) ammonium sulphate; (2) calcium cyanamide; (3) dried blood; (4) fish; (5) cotton-seed meal; (6) bone-meal; (7) fresh cow manure (solid and liquid); (8) fresh cow manure (solid); (9) leached cow manure, and (10) horse manure. The following percentages of nitrogen as (*a*) ammonium and (*b*) nitric acid were found:

	1	2	3	4	5	6	7	8	9	10
(*a*)	—	—	16·7	47·2	5·0	16·7	32·6	5·4	11·6	7·1
(*b*)	78·5	52·6	26·1	26·2	30·6	12·3	12·7	9·5	4·5	8·8

Addition of sodium nitrate (0·2 gram) to soil (100 grams) resulted in increased accumulation of nitrates followed by a decrease. Subsequently there was a further increase, and at the end of eight weeks the increased accumulation was about 13 mg. per 100 grams. With 0·6 gram of sodium nitrate the increase was still greater.

N. H. J. M.

The Co-operation of Micro-organisms in the Utilisation of the Insoluble Phosphates of the Soil (II) by Higher Plants. SANTE DE GRAZIA (*Chem. Zentr.*, 1910, i, 294; from *Arch. Farm. sperim.*, 1909, **42**, 589—606).—The authors show that factors other than micro-organisms play a part in making soluble the insoluble phosphates of the soil. The addition of chloroform to a culture, in order that only the ferment actions should be brought into play, causes diminished acidity of the culture (200 c.c. of water, 10% of dextrose, 5% of dried turf and calcium phosphate). In spite of this, the amount of dissolved phosphate is increased. The fact is explained on the assumption of enzyme activity, which hydrolyses the normal phosphate into the mono- and di-calcium salt and calcium hydroxide; the latter neutralises part of the acid of the culture medium.

S. B. S.

Decomposition of Cyanamide by Fungi. H. KAPPEN (*Centr. Bakt. Par.*, 1910, ii, **26**, 633—643).—Experiments with various fungi showed that five have the power of decomposing dilute solutions of cyanamide. Two of the fungi decompose 0·2% solutions, whilst the

other three fail to grow in solutions containing only 0·1%. The decomposition of cyanamide takes place in solutions containing very small amounts of organic matter. In the case of three of the fungi, the first product of decomposition is urea, and this is more or less converted into ammonia.

The fungi which decompose cyanamide are unable to utilise dicyanodiamide as source of nitrogen. N. H. J. M.

Hydrolysis of Racemic Amino-acids by Fungi. HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 96—109).—The study of the growth of a variety of mould fungi on racemic leucine and glutamic acid solutions shows that both optically active components are attacked. In about one half the cases studied, the attack was symmetrical; in the remainder one isomeride was preferentially attacked. In all cases this was the naturally-occurring form, and in no instance was *d*-leucine selected even by moulds obtained by exposure of *l*-alanine or *l*-alanine and dextrose solutions to the atmosphere. It is probable that there are no micro-organisms which preferentially select the antipodes of the natural amino-acids.

The presence of dextrose as an alternative source of carbon favours, as a rule, selective attack. Leucine is an excellent source of both carbon and nitrogen for a variety of fungi ; *l*-glutamic acid serves as a very suitable pabulum for *Aspergillus niger*. E. F. A.

Detection of Intracellular Ferments. EMIL ABDERHALDEN and HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 180—184).—The pressed juices of fungi, prepared by the Buchner method, are in many cases unable to effect hydrolysis of the polypeptides which are hydrolysed by the mycelium of the fungus. In such cases the pressed cake of tissue and kieselguhr is usually able to hydrolyse silk peptone solution, and it is advisable always to test the enzymic activity of both juice and residue.

dl-Leucylglycine was only hydrolysed by *Aspergillus Wentii*, *Fusarium vasinfectum*, and *Sclerotinia sclerotiorum* out of fourteen varieties of mould fungi tested ; these were mostly unable to hydrolyse glycyl-*l*-tyrosine, but attacked silk peptone. E. F. A.

Action of Arsenates on the Growth of Algæ. JOSEPH COMÈRE (*Bied. Zentr.*, 1910, **39**, 212 ; from *Bul. Soc. bot. France*, 1909, **56**, 147—151).—Experiments in which *Stichococcus flaccidus* and *Spirogyra crassa* were gradually supplied with potassium arsenate in the place of phosphate showed that the arsenate was assimilated, and the conclusion is drawn that potassium arsenate, in suitably increasing amounts, can be substituted for phosphorus as a nutrient. *Stichococcus* is much better able than *Spirogyra* to resist the action of different solutions, and in the experiment referred to, assimilated much more of the arsenate.

Previous experiments with *Oedogonium capillare* gave negative results. N. H. J. M.

Circumstances Favouring the Formation and Destruction of Acetaldehyde in Alcoholic Media. J. AUGUSTE TRILLAT and BENJAMIN SAUTON (*Bull. Soc. chim.*, 1910, [iv], **7**, 244—249).—A résumé of work already published (Abstr., 1908, ii, 615, 722; 1909, ii, 429, 606, 607; this vol., ii, 232). W. O. W.

The Content in Organic Phosphorus and the Relationship between Amide Nitrogen and the other Nitrogenous Forms (excluding Protein Nitrogen) in Ripe Seeds. A. PARROZZANI (*Chem. Zentr.*, 1910, i, 545; from *Staz. sperm. agrar. ital.*, 1909, **42**, 890—901).—The author estimated total nitrogen, protein nitrogen, amide nitrogen, amino-acid nitrogen, as well as total phosphorus, phosphoric acid, and nuclein and lecithin phosphorus. He believes that constant relationship exists between the amount of organic phosphorus and the ratio of the amide nitrogen to the other forms of nitrogen. S. B. S.

Influence of Phosphates on the Respiration of Plants. N. N. IVANOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1910, 303—318 *).—The author's measurements of the amounts of carbon dioxide evolved by wheat embryos and etiolated bean shoots of ten to twelve days' growth in presence or in absence of varying proportions of disodium hydrogen phosphate (or potassium dihydrogen phosphate) lead to the following conclusions. The respiration of the living shoots is not stimulated by 1—2% of disodium hydrogen phosphate. In the case of dead (frozen) shoots, respiration is increased to the extent of 27% by 1%, and of 62% by 2% of the phosphate. The increase in the amount of carbon dioxide liberated in the latter case takes place at the expense of the primary anaerobic process, as it also occurs in a current of hydrogen; the phosphate has no influence on the evolution of carbon dioxide by the secondary oxidising process. The increased development of carbon dioxide cannot be regarded as due to an irritant action of the phosphate, since it is observed with the dead material. T. H. P.

Action of Poisons on the Respiration of Plants. Theoretical Part. WLADIMIR I. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1910, [vi], **4**, 401—421).—The author discusses the literature on this question and draws the following conclusions.

The intense stimulation of the respiration of living plants produced by poisonous substances discontinues when the plant dies. This stimulation is not a result of the direct action of the poison on the respiratory enzymes. The living organism may resist the injurious influence of the poison on respiration and enzyme action, but dead plants are incapable of doing so. The marked stimulation of respiration by quinine is not accompanied by increase in the quantity of peroxydase present. The injurious effect of urethane on respiration is accompanied by diminution of the amount of peroxydase, but the destruction of peroxydase occurs only after, or at the time of, death. For the stimulation of the respiration of living plants by poisonous substances, the presence of oxygen is necessary. When plants with

* and *Biochem. Zeitsch.*, 1910, **25**, 171—186.

stimulated respiration are placed in an atmosphere deprived of oxygen, the increased development of carbon dioxide continues for some time, but subsequently poisoning by the poison intervenes, and a considerable fall in the quantity of carbon dioxide evolved. Living plants, which are first placed in an oxygen-free atmosphere and then subjected to the action of a poison, are not in a condition to exhibit increased energy of respiration, but suffer poisoning. The stimulation of the respiration of living plants by a poison is one of the signs of the resistance of the plant to the poison; the success of this resistance requires favourable conditions, such as a medium temperature and presence of oxygen.

Poisons act on the protoplasm, and, as a result of this action in the living plant, a whole series of reactions take place in the living plant, and may ultimately produce either intensification or weakening of the respiration. The action of a poison on the respiration of living plants is hence indirect, direct action being possible only with dead plants. The poison acts not as a catalyst or lubricant, but as a disengaging hook. Stimulation of respiration by poisons depends on increased transformation of respiratory pro-enzyme into enzyme. T. H. P.

Fermentative Ammonia Cleavage in Higher Plants. ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1910, **65**, 283—284. Compare Abstr., 1909, ii, 694).—Polemical. A reply to Butkewitsch (Abstr., 1909, ii, 1046). W. D. H.

The Changes Taking Place in the Composition of Fruits which Ripen after being Gathered. RICHARD OTTO and W. D. KOOPER (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 328—330. Compare this vol., ii, 233).—When medlars (*Mespilus germanica*) were frozen and then kept for eight days, considerable changes took place in the composition of the fruit. The invert sugar decreased from 41·13% to 37·47%; the total acidity (as malic acid) from 4·36% to 3·50, and the nitrogen from 3·08% to 2·68 per cent, all these figures being calculated on the dry substance. In the case of Japanese quinces (*Cydonia Japonica*) kept for a similar period, the sucrose (amounting to 2 0%) disappeared entirely, whilst the invert sugar decreased from 14·91% to 11·45%; the total acidity (as malic acid) decreased from 24·11% to 21·76%, and the tannin from 3·82% to 3·23%, calculated on the dry substance. After being kept for a further eleven days, the invert sugar was reduced to 7·60%, the acidity to 12·71%, and the tannin to 1 84%. W. P. S.

Amount of Acid in, and Resistance to Acids of, Different Roots. KEIJIRO ASŌ (*Flora*, 1910, **100**, 311—316. Compare Maxwell, *Landw. Versuchs-Stat.*, 1898, **50**, 325).—The results of water-culture experiments with various plants showed that spinach, mustard, and peas were greatly injured by 0·01% citric acid solutions, and that the injurious action is somewhat slower in the case of lupins, barley, oats, and potatoes

The relative acidity of the different roots was determined indirectly by means of 0·1% solutions of sodium nitrite, the injurious action of which largely depends on the amount of acid in the root hairs. The

results indicate that the plants which show the greatest root acidity are those which were best able to resist the action of dilute citric acid.

N. H. J. M.

Preparation of Aqueous Soluble Compounds from the Leaves of White Birch Trees ("Betula alba"). GEORG R. GRASSER and KARL PURKERT (D.R.-P. 217559).—When the dried leaves of the white birch (*Betula alba*) are extracted with alcohol, a resin acid, $C_{40}H_{70}O_5$, is obtained; this when treated with alcoholic alkali yields a phenolic *acid*, $C_{33}H_{65}O_2{\cdot}C_6H_3(OH){\cdot}CO_2H$, the alkali salt of which when treated with carbon dioxide furnishes the *acid*, $C_{33}H_{65}O_2{\cdot}C_6H_2(OH)(CO_2H)_2$. The *salt*, $C_{41}H_{67}O_7K_3$, is a dark green powder, odourless, with an acid taste, and soluble in water.

These compounds are of great therapeutic value, and the impure product has in the past found considerable employment in pharmaceutical preparations.

F. M. G. M.

Some of the Organic Bases Present in Cabbages. K. YOSHIMURA (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 253—256).—The following bases were found to be present in cabbage (*Brassica oleracea*), the inner part, or heart, of the cabbage being employed for the investigation: arginine, 0·0014%; lysine, 0·0004%; choline, 0 0006%; betaine (?), 0·0002%; histidine was also present.

W. P. S.

Chemical Composition of Cranberries, Whortle-berries, etc. CONSTANT GRIEBEL (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 241—252).—Analyses are given of the berries of various members of the *Vacciniaceae* order. Cranberries (*V. Vitis Idaea*), whortle-berries (*V. Oxycocos*), and American cranberries (*V. macrocarpum*) were particularly examined in order to ascertain whether benzoic acid occurred naturally in the berries.

From 0·054 to 0·144% of free benzoic acid was found to be present in cranberries, and from 0·011 to 0·041% in the other kinds. In addition, benzoic acid was present in the form of a glucoside (vacinin); the total amount of benzoic acid varied from 0·088 to 0·224% in the case of cranberries, and from 0·021 to 0·061% in whortle-berries and American cranberries. The formation of benzoic acid takes place only when the berries begin to turn red, and increases as the ripening proceeds. The glucoside is present in cranberries to the extent of about 0·1%; it has a composition corresponding with the formula $C_6H_{11}(C_6H_5{\cdot}CO)O_6$, and forms an insoluble phenylhydrazone, m. p. 135—136°. Cranberries contain a little more sugar, and less acid than the other fruits mentioned.

W. P. S.

Coffee. III. K. GORTER (*Annalen*, 1910, **372**, 237—246. Compare Abstr., 1908, i, 186, 345).—The acid isolated from Liberian coffee in a recent investigation (*loc. cit.*) has been identified as citric acid. It has also been found possible to isolate trigonelline, the presence of which in Arabian coffee has been established by Polstorff (compare

this vol., ii, 234); it is probable that Palladino's coffearine is trigonelline.

In preparing coffee-beans for the market, it is usual to allow them to ferment in order to facilitate the removal of the slimy layer from the parchment. As a result of the investigation of this process, it is found that the separation of the slimy layer from the parchment is brought about through the agency of lactic acid formed during the fermentation. The lactic acid fermentation is accompanied by alcoholic and butyric acid fermentation, but it is the lactic acid which causes the slimy layer to swell, and thereby render possible its removal by washing. W. H. G.

Corydalis aurea. GEORG HEYL (*Apoth. Zeit.*, 1910, No. **17**, *Reprint*).—From the extract obtained by treating the finely powdered rhizomes, stalks, and leaves of *Corydalis aurea* with 80% alcohol containing a little acetic acid, a *base*, m. p. 148—149°, has been isolated, which is purified through the hydrobromide, is precipitated by the usual alkaloidal reagents, and exhibits the following colour reactions: nitric acid, D 1·3, colourless and then faintly yellowish-red; Erdmann's reagent, colourless; Fröhde's reagent, olive-green, slowly becoming bluish-grey; Mandelin's reagent, olive to brownish-green. C. S.

Alkaloids of Corydalis solida. GEORG HEYL (*Apoth. Zeit.*, 1910, No. **5**, *Reprint*).—The crude alkaloids obtained from the tubers of *Corydalis solida*, collected at the end of April in the flowering season, have been purified and separated by means of their hydrobromides; a *base*, m. p. 145°, another *base*, m. p. 132—133°, and protopine, m. p. 207°, have been isolated. The hydrochloride, $C_{20}H_{19}O_5N,HCl$, and the platinichloride of the last have been analysed. C. S.

The Chemical Composition of the Fig (Ficus carica). RAFFAELE PALLADINO (*Biochem. Zeitsch.*, 1910, **24**, 263—265).—Analyses of the pulp and rhind of fresh figs and of dried figs are given, the following constituents being estimated: water, nitrogenous substances, fats, sugars, cellulose, ash, gums, and mucilaginous matter. S. B. S.

Fruit of Ilicioides mucronata. CAROLINE WILCOX (*Chem. News*, 1910, **101**, 169).—The dry, currant-like fruits contain 21·6% of reducing sugars (fructose), 1·9% of a viscid, pale yellow oil consisting of a palmitate, and 2·18% of ash. Oxalic and tartaric acids are also present. T. A. H.

The Mushroom, an Indole-yielding Plant. M. LÖWY (*Chem. Zeit.*, 1910, **34**, 340).—The blue coloration obtained with sulphuric acid (this vol., ii, 168) is due to the presence of indican. The author has detected this in both aqueous and alcoholic infusions of mushrooms. The test succeeds best by adding strong hydrochloric acid, and then a particle of ammonium persulphate. If to the extracts are added a few

drops of hydrochloric acid, and then, carefully, sulphuric acid, a dark blue liquid is obtained. Animal charcoal should not be used to decolorise brown solutions, as this removes the indican.

The indican is probably derived from the horse manure and urine applied to the mushrooms. L. DE K.

Variations in the Proportions of Oleoeuropein in the Olive from its Appearance to Maturity. ÉMILE BOURQUELOT and J. VINTILESCO (*J. Pharm. Chim.*, 1910, [vii], 1, 292—296. Compare Abstr., 1908, i, 904; Power and Tutin, Trans., 1908, **93**, 891, 904).—Power and Tutin's failure to obtain oleoeuropein as a chemical individual (Abstr., 1909, ii, 427) is due to the fact that they employed an alcoholic extract of the dried leaves. The amount of the glucoside diminishes during vegetation, and is entirely absent from the dry article of commerce. The sugar produced by hydrolysis with emulsin has been isolated and identified with dextrose. W. O. W.

Development of a Bulbous Plant. Variations in the Weight of Nitrogen and Mineral Matters. GUSTAVE ANDRÉ (*Compt. rend.*, 1910, **150**, 713—715. Compare this vol., ii, 334).—The author gives results of the analysis of the bulbs and aerial parts of dried onions at different stages of the plant's growth, and discusses the significance of variations in connexion with the development of different parts of the plant. The proportion of dry organic matter, total ash, total nitrogen, phosphoric acid, and of the oxides of magnesium, calcium, and potassium is shown in tabular form. W. O. W.

Composition of Protein from the Seeds of Pinus Koraiensis. K. YOSHIMURA (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 257—260. Compare Abstr., 1905, i, 846).—On hydrolysis with acids, the protein obtained from the seeds of *Pinus Koraiensis*, a tree growing in Central Japan, yielded tyrosine, 2 5%; leucine, 11·4%; glutamic acid, 2·7%; histidine, 0·53%; arginine, 7·05%; and lysine, 0·89%. W. P. S.

The Hydrogen Cyanide in Sambacus. CIRO RAVENNA and MARIO TONEGUTTI (*Chem. Zentr.*, 1910, i, 544; from *Staz. sperim. agrar. ital.*, 1909, **42**, 855—879).—The enzyme which decomposes the glucoside sambunigrin from *Sambucus nigra* is not soluble in water. The hydrogen cyanide in this plant is combined in the glucoside, and exists in greater quantities than has hitherto been suspected, chiefly in the stem. It is not derived, as in the case of *Sorghum vulgare*, from carbohydrates and nitrates. S. B. S.

Secretion of Salts by the Leaves of Statice Gmelini. JOHANNES SCHTSCHERBACK (*Ber. deut. bot. Ges.*, 1910, **28**, 30—34).—*Statice Gmelini*, *S. tatarica*, *Tamarix gallica*, *Frankenia pulverulenta*, and *F. hirsuta* all secrete salts from the leaves. No, or very little, secretion is observed in the case of *Statice latifolia*, whilst with *S. Gmelini* the secretion is so considerable that the plants will thrive in soils containing enormous amounts of soluble salts. The salts accumulate on the leaves in the form of curled threads.

When the stems of freshly-cut leaves of *Statice Gmelini* are placed in distilled water, the secretion of salts continues for three days, and secretion of water for a week. With 5% solutions of sodium chloride, 1% sodium sulphate, 1% dipotassium hydrogen phosphate, 3% sodium sulphite, 1% mannitol, a saturated solution of asparagine, and 4% urea, the secretion was as vigorous, or nearly so, as with water. The chlorides and sulphates of sodium, potassium, and magnesium are the most favourable to secretion, whilst calcium compounds and sugar have an inhibiting effect. With 4% sucrose solutions the secretion was the same as with water, but no sucrose could be detected. In the case of inulin (2%) the secretion was less than with water. N. H. J. M.

Physiological Meaning of the Hairs of Stellaria media. LEOPOLD KNY (*Ber. deut. bot. Ges.*, 1909, **27**, 532—535).—According to results obtained by Jamieson (*Rep. Agric. Research Assoc.*, 1905), the hairs of *Stellaria media* and *Spergula arvensis* contain large amounts of proteins, first at the ends and later in the lower portions. The conclusion was drawn that free atmospheric nitrogen is absorbed and assimilated by the hairs.

The examination of hairs of *Stellaria media* by means of all known reagents for protein gave negative results, and no indication was obtained of any fixation of free nitrogen. N. H. J. M.

Cyanogen Compounds in Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1910, **34**, 298—299).—The tobacco smoke was passed through aqueous sodium hydroxide containing ferrous hydroxide in suspension, and the ferrocyanide formed was precipitated with copper sulphate after neutralisation with nitric acid. The iron contained in the precipitate represents cyanogen. The smoke from the cigars tested contained on an average 0·09% of dicyanogen.

From the results of a previous research (Abstr., 1909, ii, 839), the presence of free hydrocyanic acid is out of the question. L. DE K.

Presence of Boron in Algerian Wines. J. DUGAST (*Compt. rend.*, 1910, **150**, 838—839. Compare Crampton, Abstr., 1889, 797; Azzarello, Abstr., 1907, ii, 125).—Traces of boron have been found in different organs of Algerian vines, notably in the branches, and in the skin and stones of the fruit. W. O. W.

New Method for Combating Mildew by means of Copper Oxychloride. ERNEST CHUARD (*Compt. rend.*, 1910, **150**, 839—841). —The substitution of copper oxychloride for copper sulphate in viticulture diminishes the amount of copper salt required. The oxychloride probably undergoes slow oxidation on the leaf, and the cupric chloride produced being easily ionised, the substance is more effective than other insoluble copper compounds, such as the hydroxide or carbonate. W. O. W.

Lead Arsenate in Viticulture. L. MOREAU and E. VINET (*Compt. rend.*, 1910, **150**, 787—790).—Lead arsenate employed as an insecticide is present in the grapes at harvest, but is absent from the wine, probably owing to elimination with the skins and lees.

W. O. W.

Composition of Some Bengali Food Materials. HOPE SHERMAN and H. L. HIGGINS (*J. Amer. Chem. Soc.*, 1910, **32**, 558—561).—The percentages of water, nitrogen, protein, and fat in several Bengali food-stuffs, including wheat, maize, rice, and various pulses, have been estimated, and the results are compared with those given by similar American products. The heats of combustion are also recorded. E. G.

Effects of Soluble Salts on Insoluble Phosphates. J. E. GREAVES (*J. Biol. Chem.*, 1910, **7**, 287—319).—Various authorities have studied the effect of salts on the fertility of soils, and a complete résumé of the results obtained is given (compare Dyer, Trans., 1894, **65**, 115; *Phil. Trans.*, 1901, *B*, **194**, 235). The author has compared the solubilities of certain natural phosphates (both weathered and unweathered) in distilled water and in dilute saline solutions. The results prove that sodium, potassium, and magnesium sulphates and all ammonium compounds extract more phosphorus compounds from the weathered phosphate than is extracted by distilled water. All the calcium and iron compounds and sodium nitrate diminish the solubility of the phosphate; magnesium, sodium, and potassium chlorides and potassium nitrate have practically no effect.

With an unweathered phosphate, the following salts have the greatest effect in increasing the solubility of the phosphate: ammonium salts, magnesium sulphate, and potassium nitrate. When soil is mixed with the phosphate, the addition of ammonium chloride or magnesium sulphate diminishes the solubility of the phosphate, but in many cases, especially with ammonium nitrate, the presence of soil with the phosphate causes the solvent to act more vigorously.

Sodium and potassium nitrates render calcium phosphate more soluble, but iron phosphates less soluble. J. J. S.

Occurrence of Manganese in Soil, and its Effect on Grass. FREDERICK B. GUTHRIE and L. COHEN (*Agric. Gaz. N.S. Wales*, 1910, **21**, 219—222).—Analyses of soil from bare patches in grass laid down five years previously showed the presence of manganese (Mn_2O_3 = 0·254%), whilst other portions of the soil were found to contain no manganese. The analyses showed no other differences in the various portions of the soil. The toxic action is most marked in the winter, when the plants are less vigorous.

Other cases are mentioned in which the failure of barley and wheat was found to be coincident with higher percentages of manganese in the sterile land than in the adjacent normal soil.

It is suggested that the manganese may be originally present in innocuous forms, which become toxic by oxidation. N. H. J. M.

Amount of Nitrogen in Rain-water Collected at Flahult, Sweden. HJALMAR VON FEILITZEN and IVAR LUGNER (*Fühling's Landw. Zeit.*, 1910, **58**, 248—252, and *Kungl. Landtbr.-Akad. Handl. Tidskr.*, 1910, 151—157. Compare Shutt, Abstr., 1909, ii, 429, and Seton, *ibid.*, ii, 340).—Analyses of monthly samples of rain and snow

collected from January to December, 1909. The average results for the year are as follows:

	Nitrogen per million.		Nitrogen per acre (lbs.)			% of total N.	
Rainfall inches	as ammonia	as nitrates	as ammonia	as nitrates	Total	as ammonia	as nitrates
32·55	0·450	0·177	3·317	1·302	4·619	71·8	28·2

The rain-water can only be contaminated to a very slight extent, as the nearest town, Jönköping, is ten miles north of Flahult, whilst the prevailing winds are from the south and south-west. The rainfall in 1909 was about 40% higher than the average of the last seven years.

N. H. J. M.

Analytical Chemistry.

Substitute for Platinum Wire in Qualitative Analysis. OSWALD F. KIRBY (*Chem. News*, 1910, **101**, 170).—A few asbestos threads, about 12 cm. in length, are dipped into a solution containing one part of phosphoric acid in two of water, and gently heated in a Bunsen flame until the greater part of the water has evaporated. The threads are then rolled together between the fingers to form a filament of 2—3 mm. cross section, which is then heated in a flame until it is converted into a porcelain-like rod. Such rods may be used for the observation of flame coloration tests, borax beads, etc. T. A. H.

Modified Hempel Burette. A. GWIGGNER (*Zeitsch. angew. Chem.*, 1910, **23**, 642).—The new burette is furnished at the top with a three-way stopcock, the openings of which are separated from each other by 120°, thus establishing a simple communication with the outer air or the gas pipettes, or enabling the communication to be shut off during the absorption process. The communication with the pipette is established by means of a capillary tube bent upwards. Below the lower three-way-cock, the burette is ground into a bottle connected by a flexible tube with an acid reservoir. In order to fill the burette, the gas is passed for some three minutes, the lower stopcock is turned, and the gas in the tubes below it is expelled by raising the reservoir, which is filled with acidified water coloured with methyl-orange.

The extra pressure in the burette is relieved in the usual manner (supposing that the burette has been filled from stock gas bottles under pressure). After establishing the communication with the pipette by means of a capillary tube bent twice at right angles, the air contained in the latter may be expelled completely by the absorption liquid, which is pressed as far as the stopcock of the burette.

L. DE K.

A New Indicator, α-Naphtholphthalein, which Changes in the Neighbourhood of the Neutral Point. SÖREN P. L. SÖRENSEN and S. PALITZSCH (*Biochem. Zeitsch.*, 1910, **24**, 381—386).—The authors describe the method of preparation of this indicator from α-naphthol and phthalyl chloride. It was purified by recrystallisation from benzene in a Soxhlet apparatus. The indicator solution is made by dissolving 0·1 gram in a mixture of 150 c.c. of alcohol and 100 c.c. of water. The change is marked between $p_H = 7·26$ and $p_H = 8·68$. The indicator is not suitable for solutions containing the natural proteins.
S. B. S.

Rapid Electro-analysis with Stationary Electrodes. T. SLATER PRICE and T. C. HUMPHREYS (*J. Soc. Chem. Ind.*, 1910, **29**, 307—309).—An investigation as to the merits of Stoddard's process (Abstr., 1909, ii, 347).

The authors give it as their opinion that for rapid analysis, stationary electrodes are not so satisfactory as rotating electrodes, particularly so in the case of silver or zinc. A great disadvantage is that a tap-funnel cannot be used to hold the electrolyte, owing to some of the latter remaining in the neck of the funnel, thus escaping electrolysis. L. DE K.

Potassium Hydroxide Containing Paraffin and Colourless Alcoholic Potassium Hydroxide Solution. F. BENGEN (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 269—271).—Having noticed that potassium hydroxide occasionally yields oily drops when dissolved in alcohol, the author separated this oily matter, and found that it consisted of a paraffin having the properties of *paraffinum liquidum*. The sticks of potassium hydroxide had apparently been coated with a thin layer of paraffin. By dissolving 1000 grams of the hydroxide in water and extracting the solution with ether, 0·544 gram of the paraffin was obtained. It is obvious that such potassium hydroxide could not be used for certain analytical processes, such as the estimation of unsaponifiable matters in fats, the phytosteryl acetate test, etc. As regards the preparation of alcoholic potassium hydroxide solution, the author states that, to obtain a solution which will remain colourless, alcohol should be used which has been stored in glass vessels. Alcohol which has been kept in wooden barrels always gives a coloured solution with alkalis, but may be purified by slow distillation after treatment with recently-fused potassium hydroxide. W. P. S.

Three Laboratory Instruments. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1910, **49**, 295—298).—The author describes (I) a stock bottle for carbon disulphide; (II) a separating tube on the principle of the ordinary wash-bottle, and (III) a bottle for supplying ammonia vapour when this is required for colour reactions. L. DE K.

Various Short [Analytical] Communications. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, **24**, 423—442).—I. *Polarisation.*—A convenient method of obtaining a bright sodium light consists in the use of sodium nitrite in the flame.

II. *Clearing and Decolorising Solutions.*—The author has obtained satisfactory results with colloidal iron hydroxide solution, and also

with *liquor ferri subacetici.* When it is desired to avoid the addition of fresh liquid, kieselguhr or kaolin can be employed; the former is to be preferred. In cases where urine is to be polarimetrically examined, the author finds that lead acetate, in solutions slightly acidified with acetic acid, gives results as satisfactory as those obtained with mercuric nitrate employed by various French chemists. Neither of these reagents is applicable to urines containing large quantities of amino-acids and other abnormal products; in this case he recommends the use of mercuric acetate.

III. *Some Reactions of Fermented Sugar Solutions.*—After concentration, sugar solutions in which the sugar has been completely fermented are still optically active, sometimes dextrorotatory and sometimes lævorotatory, although not capable of directly reducing Fehling's solution without hydrolysis. The author concludes, from the result of several tests, that the optical activity is due to a complex mixture of substances, probably derived from the autolysis of yeast.

IV. *Bismuth Hydrogen Iodide as a Precipitant of Bases.*—The author prefers the barium and ammonium salts of this iodide to the potassium salt as ordinarily used, owing to the greater ease with which the bases can be regenerated. He gives details as to the preparation of the reagents.

V. *The Method of Carrying out Kjeldahl Estimations.*—When mercury is used, the author recommends the employment of potassium xanthate instead of sodium thiosulphate for decomposing the amidomercuric sulphate formed.

VI. *Experiences with the Naphtharesorcinol Reaction.*—The author reiterates his experiences with this reagent, showing that the reaction is given by other substances than glycuronates. The reagent itself alters in light. The reaction is, furthermore, interfered with by the presence of other substances, such as dextrose, formaldehyde, and acetaldehyde, and substances generally which contain the carbonyl group. In these cases a large excess of the reagent should be employed.

VII. *The Increase of the Sensibility of the Tryptophan Reaction.*—After addition of the solution of halogen, the mixture is extracted with ethyl acetate, and the colour passes into the organic solvent. The shade is slightly different from that in aqueous solution.

S. B. S.

Volumetric Estimation of Hydrogen Peroxide in the Presence of Persulphuric Acid. ANTON SKRABAL and J. P. VACEK (*Chem. Zentr.*, 1910, i, 961; from *Oesterr. Chem. Zeit.*, 1910, [ii], 13, 27—29).—The joint available oxygen is estimated by adding dilute sulphuric acid and an excess of standard ferrous sulphate; after adding an equal bulk of boiling water, the excess of ferrous iron is titrated with standard permanganate. The same quantity of the solution is mixed with a solution of to 5 to 3 grams of manganous sulphate, dilute sulphuric acid is added, and then permanganate until an abundant deposit of manganese peroxide has formed. When the evolution of gas ceases, excess of ferrous sulphate is added, and, after diluting with boiling water, the excess of iron is titrated with permanganate.

L. DE K.

Estimation of Chlorates in the Presence of Nitrates and Chlorides. TARAK NATH DAS (*Chem. News*, 1910, **101**, 158).—A slight but essential modification of the process recommended previously (this vol., ii, 238). The alkaline liquid in the flask, to which phenolphthalein has been added, is just neutralised with the acid from the dropping funnel before the iodine solution is allowed to regurgitate into the flask. Any free acidity should be neutralised with a mixture of sodium hydrogen carbonate and potassium sodium tartrate.

L. DE K.

Colorimetric Estimation of Small Quantities of Bromine in the Presence of Large Quantities of Chlorine and Small Quantities of Iodine. WILLIAM J. DIBDIN and LEONARD H. COOPER (*Analyst*, 1910, **35**, 159—161).—*Estimation of Bromine.*—A convenient quantity of the liquid to be tested is placed in a 100 c.c. Nessler glass, 10 c.c. of 50 vol. % sulphuric acid are added, and then saturated chlorine water drop by drop until the maximum coloration is obtained. If a brown coloration due to iodine is noticed, more chlorine water is added until it disappears. The depth of the colour due to bromine is then matched by means of standard potassium bromide (0·001 gram of bromine per c.c.), treating this in exactly the same way as the sample.

Estimation of Iodine in the Presence of Bromides and Chlorides.—To a convenient portion of the liquid contained in a Nessler glass are added 10 c.c. of the above sulphuric acid, and bromine water (2 c.c. of bromine dissolved in 200 c.c. of hydrochloric acid; 20 c.c. of this are diluted to 1 litre) is cautiously added until the maximum brown coloration is obtained. The colour is then matched by means of a standard iodide solution (0·0001 gram of iodine per c.c.). L. DE K.

[Method of Estimating very Small Amounts of Nitrogen.] EILHARD A. MITSCHERLICH (*Landw. Versuchs-Stat.*, 1910, **72**, 459—464).—A reply to Zeller (this vol., ii, 70). N. H. J. M.

Estimation of Nitrogen in Foods with Different Amounts of Substance. OTTO ENGELS (*Landw. Versuchs-Stat.*, 1910, **72**, 407—412).—A large number of nitrogen determinations in different foods were made by the usual Kjeldahl method, employing in each case 1, 2·5, and 5 grams of substance. When the larger amounts were used, the decomposition was carried out in round 500 c.c. flasks. After heating, the contents were diluted to 500 c.c., and aliquot portions distilled, instead of the whole, as when only 1 gram of substance was employed.

With oil cakes and meals, the differences were not great with 1 gram of substance. In the case of other substances, such as brewers' grains and malt germs, the errors (with 1 gram) were, however, considerable, being sometimes more than 2% or 3%.

The following method is recommended: The substance (2·5 grams, or sometimes 5 grams) is heated in a round 500 c.c. Jena flask with 35 c.c. of sulphuric acid and the usual amount of mercury until

white fumes are visible. Pure potassium sulphate (15—18 grams) is then added, and the heating continued for forty-five minutes or an hour. An aliquot portion of the diluted solution is then distilled, the remainder being reserved in case of accident until the analysis is completed. N. H. J. M.

Application of the Folin Method to the Determination of the Ammoniacal Nitrogen in Meat. MARY E. PENNINGTON and A. D. GREENLEE (*J. Amer. Chem. Soc.*, 1910, **32**, 561—568).—The quantity of loosely-bound nitrogen in meat has long been recognised as an indication of its freshness, but the methods of estimating it have hitherto been unsatisfactory. It is now shown, however, that the so-called ammoniacal nitrogen can be accurately estimated by a modification of Folin's method (Abstr., 1903, ii, 239). The meat in a finely divided state is suspended in water containing magnesium oxide or sodium carbonate, and a current of air is passed through the mixture, and afterwards through *N*/10 sulphuric acid. By this means, the whole of the nitrogen which is eliminated by weak alkali at the ordinary temperature can be removed in three to six hours.

This method has been applied to the estimation of the ammoniacal nitrogen in the flesh of fowls, and the following results have been obtained. The flesh of perfectly fresh birds yields 0·011—0·012% of ammoniacal nitrogen; that of birds kept at a moderately low temperature for four to nine days yields 0·014—0·019%, whilst that of specimens which have been in cold storage for a year or more gives a varying amount which is always much higher than that from the fresh birds. E. G.

The Method of Nitrogen Estimation in the Urine. PETER RONA and R. OTTENBERG (*Biochem. Zeitsch.*, 1910, **24**, 354—356).—After destroying the organic matter by Kjeldahl's method, the ammonia is estimated by the Schiff-Sörensen method by titration after treatment with formaldehyde. The excess of sulphuric acid is first neutralised with sodium hydroxide, using litmus as indicator, neutralised formaldehyde solution is then added, and the ammonia is then titrated after addition of phenolphthalein as indicator. The authors give the details of the manipulation. S. B. S.

Titration of Ammonia in Urine by the Formaldehyde Method; Titration of the Acidity. O. VON SPINDLER (*Chem. Zentr.*, 1910, i, 692; from *Schweiz. Woch. Chem. Pharm.*, 1909, **47**, 767—770).—The process is a combination of the methods proposed by Maly-Dénigès and by Ronchèse. Twenty c.c. of urine are mixed with 20 c.c. of *N*/10-sodium hydroxide, 5 c.c. of 10% barium chloride solution are added, and the whole diluted to 100 c.c. To 50 c.c. of the filtrate are added 10 grams of sodium chloride and 10 c.c. of *N*/10-hydrochloric acid, and the liquid is then titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator; this gives the apparent acidity. Twenty c.c. of 20% formaldehyde are now added, and the titration is continued; the acidity liberated represents the ammonia. For the

calculation of the true acidity, a correction table, given in the original article, must be consulted. L. DE K.

Estimation of Acidity and of Ammonia in Urine and Its Clinical Application. H. BJÖRN ANDERSEN and MARIUS LAURITZEN (*Zeitsch. physiol. Chem.*, 1910, **64**, 21—38).—*Direct estimation of ammonia.*—Twenty c.c. of urine are placed in a litre fractionating flask, and 20 c.c. of barium hydroxide solution are added. The flask is connected with a 10-bulb absorption tube containing 20 c.c. of *N*/10-sulphuric acid; this in turn is connected with a water air-pump. The flask is placed in a water-bath at 50°, and, after heating for fifteen to twenty minutes, about one-fourth of the liquid, and consequently all the ammonia, has passed over. The excess of acid is then titrated as usual.

Indirect estimation of ammonia by means of the ammonia-combined acidity.—Twenty c.c. of urine are mixed with five drops of 0·5% phenolphthalein solution and 20 grams of normal powdered potassium oxalate. The solution is now titrated with *N*/10-sodium hydroxide, and 5 c.c. of formaldehyde neutralised previously with *N*/10-alkali are added. This causes the liquid to turn acid, and the acidity liberated is then again titrated; this represents the acidity in the form of ammonium salt. This process does not give absolutely correct results, but in practice it is a very convenient one for controlling the increase or otherwise of the ammonia secreted by patients from day to day. L. DE K.

New and Very Delicate Colour Test for Nitric Acid and Nitrates. JULIUS SCHMIDT and HERMANN LUMPP (*Ber.*, 1910, **43**, 794—797).—The blue solution of di-9(10)-hydroxyphenanthrylamine (this vol., i, 313) in concentrated sulphuric acid (concentration of solution: 0·01 gram in 100 c.c.) forms a very sensitive reagent for nitric acid. A few particles of the substance to be tested are added to 2—3 c.c. of the reagent; if nitrates are present, the blue colour changes to a wine-red. Water destroys the delicacy of the test, so that the substance must be added as a solid, or, if liquid, it must first be treated with concentrated sulphuric acid.

The test is trustworthy, even in the presence of other oxidising agents, such as dichromates, chlorates, etc. The colours produced by the latter substances are different from, and do not mask, that given by nitrates. Small quantities of nitrites do not affect the test, but with large quantities nitric acid is produced, and the same colour is produced as with nitrates.

Solutions of 9-hydroxyphenanthrene, di-9-phenanthrylamine, and di-3-bromo-9-phenanthrylamine in concentrated sulphuric acid also give colours with oxidising agents, but the test is not so delicate as with the di-9(10)-hydroxyphenanthrylamine. T. S. P.

Detection of Nitrates in the Presence of Chlorates, Bromates, etc. ALFREDO ESPINOSA TAMAYO (*Ann. Chim. anal.*, 1910, **15**, 135).—The process given by Pozzi-Escot (Abstr., 1909, ii, 1051) is recommended.

Any ammonia present is first expelled by boiling with aqueous

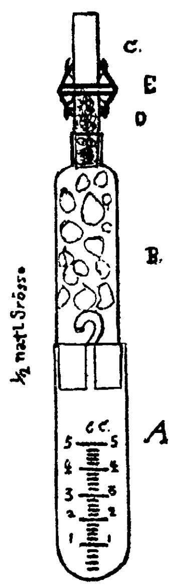
sodium hydroxide. The nitrate is then reduced to ammonia by zinc powder, as directed. L. DE K.

General Method of Estimating Nitric Nitrogen. SALLE (*Ann. Chim. anal.*, 1910, **15**, 103—105).—In a 600 c.c. flask are placed 0·5 gram of the nitrate, 200 c.c. of water, 5 grams of zinc powder, 1—2 grams of ferrous sulphate, and 50 c.c. of 36% aqueous sodium hydroxide. Inside the neck of the flask is placed a small piece of metal gauze covered with glass wool; this arrangement prevents any alkali from getting into the distillate. The flask is then connected with a condenser, and the ammonia formed on heating is distilled off and collected with standard acid. This operation generally takes thirty-five minutes. The excess of acid is then titrated as usual.

L. DE K.

Estimation of Nitrogen in Explosives. OTTO POPPENBERG and ERICH STEPHAN (*Zeitsch. Ges. Schiess- und Sprengstoffwesen*, 1909, **4**, 350—251. Compare Abstr., 1903, ii, 328).—The powder is mixed with copper oxide, enclosed in a small iron bomb in an atmosphere of carbon dioxide and heated, the decomposition products, which contain hydrogen and carbon monoxide, are passed into a tube filled with copper oxide and burnt in a stream of carbon dioxide, and the nitrogen finally collected in a graduated vessel over potassium hydroxide. A sketch of the apparatus, with full details, is given in the paper. F. M. G. M.

Apparatus for Estimating [Traces of] Arsenic. H. KASARNOWSKI (*Chem. Zeit.*, 1910, **34**, 299).—The graduated tube *A* is the recipient for the acid, zinc, and substance to be examined for traces of arsenic. The centre part *B*, ground to *A*, serves as a wash-bottle, and contains a 10% solution of lead acetate; on the top, pieces of pumice drenched with the same solution are placed: any hydrogen sulphide is thus removed. The top part, *C* and *D*, consists of two glass tubes, which serve to hold the mercuric chloride test papers, and the flattened, ground edges are held together by india-rubber rings passing over hooks, as shown in the figure.



The lower tube *D* is ground into *B*, and carries a plug of cotton-wool moistened with lead acetate to remove the last traces of hydrogen sulphide.

The yellow or reddish-brown coloration of the test papers at the end of the experiment gives a a fair idea as to the amount of arsenic present (Gutzeit's test).

L. DE K.

Marsh Test and Excess Potential. I. Quantitative Determination of Arsenic. W. D. HARKINS, (*J. Amer. Chem. Soc.*, 1910, **32**, 518—530).—Parsons and Stewart (Abstr., 1903, ii, 103)

have shown that the addition of iron salts to the liquid to be tested by the Marsh method interferes with the estimation, owing to the retention of some of the arsenic by the iron. The experiments of these authors have now been repeated and their results confirmed. The investigation has been extended to the influence of other salts.

It has been found that salts of tin, cadmium, lead, or bismuth render the zinc active, but, unlike iron and platinum, do not decrease the reducing power. Arsenic can be separated quantitatively from iron and estimated in one process, either by heating the generating flask at 100°, or by adding a salt of tin, cadmium, lead, or bismuth. Metals of low excess potential appear to hinder the reduction, whilst metals of high excess potential do not have any injurious effect. The rate of reduction of arsenic oxides increases with the rapidity of the evolution of hydrogen, provided that the latter is not due to the presence of a metal of low excess potential. A special form of furnace is described for heating the glass tube in which the arsenic hydride is decomposed, and by means of this the accuracy of the results is considerably increased. The method is applicable to the analysis of ores and other materials containing large quantities of arsenic, and can also be used for the estimation of amounts as small as 0·001 milligram. E. G.

Assay of Perborates. EDWARD K. FARRAR (*J. Soc. Dyers*, 1910, **26**, 81—82).—A carefully prepared specimen of sodium perborate did not liberate iodine from potassium iodide, showing it to be not a true perborate, but a compound of borate with hydrogen peroxide; the ammonium salt, however, did contain a proportion of true perborate.

The assay as regards available oxygen is best carried out by adding about 0·1 gram of the sample to an acid solution of 2 grams of ferrous ammonium sulphate, and then titrating the excess of ferrous iron with standard titanous chloride, using potassium thiocyanate as indicator. Or, the perborate may be added to a definite volume of titanous chloride, the excess of which is then titrated, in an atmosphere of carbon dioxide, with standard iron alum, also using thiocyanate as indicator. L. DE K.

The Alkalinity of Sea-water. ERNST RUPPIN (*Zeitsch. anorg. Chem.*, 1910, **66**, 122—156).—The following method gives the best results in the estimation of the alkalinity of sea-water, especially on board ship. Two hundred c.c. of sea-water are introduced into a Jena glass flask with ground stopper, 15 c.c. of *N*/20-hydrochloric acid are added, and the whole boiled for several minutes to expel carbon dioxide. After cooling, 15 c.c. of *N*/20-potassium iodate and 10 c.c. of 10% potassium iodide are added. The closed flask is left in darkness for one and a-quarter hours, and the solution then titrated with *N*/50-sodium thiosulphate, freshly prepared by diluting a *N*/5-solution, which is stable. The results are expressed in c.c. of carbon dioxide per litre of sea-water. Many tables of the results obtained in the North Sea and the Baltic are given. The temperature of the sea, and the depth from which the samples are taken, have little influence on the alkalinity. The salinity has the greatest influence, oceanic water having generally an alkalinity of 27 c.c., which decreases

irregularly with increasing dilution, increasing again as the mouths of rivers are approached.

The possible errors due to the presence of salts of other weak acids are shown to be small. A discussion of the ionic concentrations shows that sea-water is neutral when containing 25 c.c. of carbon dioxide per litre. It is also shown that the properties of sea-water depending on its alkalinity may be referred to temperature, alkalinity, and total carbon dioxide as variables. C. H. D.

Estimation of Potassium. I. LUIGI ERMANNO CAVAZZA (*Chem. Zentr.*, 1910, i, 962—963; from *Alba. Scuola Vitic. Enol.*, Jan., Reprint).—A new process for estimating potassium in soils and potash-manures, based on the decomposition of chlorides by oxalic acid. Five hundred grams of dry soil are warmed on the water-bath for half an hour with 200—350 c.c. of 10% hydrochloric acid, and 20—35 c.c. of the filtrate (=50 grams of sample) are evaporated with addition of 5 grams of oxalic acid. This operation is repeated four times, until no more hydrochloric acid fumes are noticed. The residue is then ignited and weighed. The carbonates of potassium and sodium are dissolved in a little water, and the residue is again heated and weighed. The alkaline solution may then be titrated, using methyl-orange as indicator. L. DE K.

Estimation of Assimilable Potassium in Soils. BIÉLER-CHATELAN (*Compt. rend.*, 1910, **150**, 716—719).—By extracting soils with water saturated with carbon dioxide, a better measure of assimilable potassium is obtained than when the extraction is effected by hydrochloric acid. Extraction by displacement gives results which are somewhat more accurate than those obtained by the method of agitation. A tabular statement is given, showing for several varieties of soils the amount of potassium extracted by hydrochloric acid and aqueous carbonic acid respectively, and also the relative influence of the potassium on the yield of crops. W. O. W.

Estimation of Potassium Nitrate in Meat by means of Nitron. CARL PAAL and A. GANGHOFER (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 322—328).—The nitrate present in certain meats may be estimated directly by means of the nitron method (Abstr., 1905, ii, 282), without clarifying the aqueous extract of the meat with lead acetate, if sulphuric acid is added to prevent colloidal solution of the nitron nitrate (compare Abstr., 1909, ii, 517). The meat under examination should be extracted thoroughly with hot water, and the hydroxide solution, after the addition of 1·0 gram of sodium per 250 c.c. of solution, is evaporated to a small volume and rendered acid by the addition of 25% sulphuric acid. The precipitate formed is removed by filtration, and the nitrate is then estimated in the filtrate after the addition of 15 drops of concentrated sulphuric acid. W. P. S.

Estimation of Lithium in Waters. MARCO T. LECCO (*Zeitsch. anal. Chem.*, 1910, **49**, 286—287).—The filtrate from the magnesium

is evaporated in a platinum dish with sodium hydroxide more than sufficient to decompose the ammonium salts. After heating the mass for some time at 100°, it is treated with hot water and further tested by Meyer's method (recommended by Fresenius). If the mass dissolves completely in water, lithium is practically absent.

L. DE K.

The Precipitation of Calcium Oxalate. ERNST MURMANN (*Österr. Chem. Zeit.*, 1909, **12**, 305—306).—Calcium oxalate is precipitated in granular form when a hot neutral, acetic acid, or very dilute hydrochloric acid solution of the calcium salt is treated with either a hot or cold solution of oxalic acid, boiled, and slowly treated with ammonium acetate; the addition of a little alcohol to complete precipitation is recommended.

F. M. G. M.

Volumetric Estimation of Barium. ETTORE SELVATICI (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 862—864).—The following method is stated to be trustworthy for the estimation of barium hydroxide in the presence of sodium and potassium hydroxides; briefly, the barium is precipitated by the addition of an excess of potassium dichromate solution, and the excess of the latter is estimated iodometrically after the barium chromate has been removed by filtration. The solution containing the three hydroxides is treated with a small quantity of acetic acid, and a definite volume (an excess) of standard potassium dichromate solution is added. This solution is prepared by dissolving 4·66 grams of the dry salt in 1 litre of water; each c.c. is equivalent to 0·01 gram of crystallised barium hydroxide. The mixture is then diluted with water to a definite volume, and filtered. An aliquot portion of the filtrate is treated with potassium iodide and hydrochloric acid, and the liberated iodine is titrated with thiosulphate solution which has been standardised on the potassium dichromate solution. A simple calculation gives the quantity of barium hydroxide present.

W. P. S.

Useful Reactions of Zinc, Nickel, and Cobalt. EUGENIO PIÑERÚA ALVAREZ (*Ann. Chim. anal.*, 1910, **15**, 129—131).—The reagent (potassium cobaltocyanide) is prepared by dissolving 10 parts of cobalt sulphate or chloride in 100 parts of water saturated at 0° with sulphur dioxide; pure potassium cyanide is then added until the red precipitate has redissolved.

If to the reagent is added a solution of zinc sulphate containing sulphur dioxide, an intensely orange-red precipitate is formed, soluble in excess of the reagent with a dark red colour. The precipitate when dried in a current of air has an orange colour; on heating, it loses water and turns violet, but when moistened it resumes its original colour.

Nickel sulphate in presence of sulphur dioxide gives a yellow precipitate, which turns green on warming. It is also soluble in excess of the reagent with a yellow colour, which is bleached on adding tartaric acid.

Cobalt sulphate in presence of sulphur dioxide gives a red

precipitate dissolving in excess of the reagent with a dark red colour, which is not readily bleached by tartaric acid.

In ordinary analysis, the mixed sulphides of cobalt and nickel are dissolved in nitrohydrochloric acid, and the solution is evaporated to dryness. If now the chlorides are dissolved in sulphurous acid and pure potassium cyanide is added, a pale green precipitate soluble in excess of the cyanide with a yellow colour, discharged by tartaric acid, will form if nickel only is present. If the solution merely contains cobalt, a red precipitate is obtained soluble in excess of the cyanide with a red colour, which turns a permanent yellow on adding tartaric acid. If both cobalt and nickel are present, the latter being in excess, a yellowish-red precipitate is obtained, which redissolves in excess of the cyanide with a yellow colour, which is almost completely bleached by tartaric acid. If, however, the cobalt is in excess, a red precipitate and red solution are obtained, not decolorised by tartaric acid.

L. DE K.

Electrolytic Estimation of Zinc. ELLWOOD B. SPEAR, EDWARD E. WELLS, and BRAINERD DYER (*J. Amer. Chem. Soc.*, 1910, **32**, 530—533).—Price (*Chem. News*, 1906, **94**, 18; 1908, **97**, 89) has pointed out that the results obtained in the electrolytic estimation of zinc are too high. The present authors have investigated the sodium acetate, potassium oxalate, and alkali hydroxide methods, and have found that in each case when the zinc is completely precipitated, high results are invariably obtained.

Zinc can be best detected by means of potassium ferrocyanide at a temperature of 50—70°. The solution should be acidified with 10—15 c.c. of sulphuric acid of D 1·84, and potassium ferrocyanide added until the concentration is about 25 grams per litre. Under these conditions, 0·5 mg. of zinc produces a turbidity even in presence of large quantities of salts of organic acids. E. G.

Causes of the High Results in the Electrolytic Estimation of Zinc. ELLWOOD B. SPEAR (*J. Amer. Chem. Soc.*, 1910, **32**, 533—538).—It has been shown by Spear, Wells, and Dyer (preceding abstract) that the results obtained in the electrolytic estimation of zinc are invariably too high. It has now been found that this is not due to the enclosure of liquid by the deposit, to the precipitation of a salt with the zinc, to the adsorption of hydrogen or its deposition as zinc hydride, or to the presence of another metal, but is caused by the deposition of zinc oxide or hydroxide with the zinc.

The electro-deposition of zinc is discussed from a theoretical standpoint, and reasons are adduced for the rapid evolution of hydrogen in strongly alkaline solutions. E. G.

Estimation of Zinc by Weighing it as Zinc Sulphate. EUGENE C. SULLIVAN and W. C. TAYLOR (*J. Ind. Engin. Chem.*, 1909, **1**, 476).—The zinc is precipitated as sulphide from a warm solution to which small quantities of ammonium hydroxide are added during the precipitation to counteract the increasing acidity.

The precipitate is collected, washed, and redissolved in the minimum quantity of dilute hydrochloric acid, with which the filter paper must

also be carefully cleansed; the clear liquid is evaporated, transferred to a tared crucible, and treated with a slight excess of sulphuric acid, evaporated to dryness, and subsequently heated to redness.

F. M. G. M.

Formation of Rubeanic Acid in the Analytical Separation of Cadmium and Copper. HEINRICH BILTZ and WILHELM BILTZ (*Ber.*, 1910, **43**, 958—959); LOTHAR WÖHLER (*ibid.*, 1194).—The formation of rubeanic acid noted by Wöhler and Hirschberg (this vol., ii, 349) has been mentioned by H. and W. Biltz and by Treadwell in their text-books.

C. S.

Electro-analytical Determination of Lead as Peroxide. HENRY J. S. SAND (*Trans. Faraday. Soc.*, 1910, **5**, 207—211).—Lead is deposited as peroxide on rotating gauze electrodes from nitric acid solution (Trans., 1907, **91**, 397). The precipitate takes up moisture from damp air at 200°, so that it must be dried in a dry atmosphere. Temperatures much higher than 200° lead to a slow decomposition of the peroxide. A simpler plan is to dip the deposit (which is dehydrated by the electric current) at once into alcohol and then into ether, and dry it over a flame. For deposits obtained at 90° with a current of five amperes (using the author's electrodes), the factor 0·863 may be used to calculate the weight of lead in the deposit; at 95—97° the factor is 0·865, instead of the theoretical value 0·866.

T. E.

Toxicological Detection of Mercury and Mercurial Compounds. MARCO T. LECCO (*Zeitsch. anal. Chem.*, 1910, **49**, 283—284).—If a liquid mixture of animal or vegetable substances containing mercuric sulphide or globules of metallic mercury is submitted to distillation, metallic mercury does not pass over into the aqueous distillate. If, however, the mixture contains calomel or corrosive sublimate, which are reduced to metal by the organic matters or mercury in an extremely fine state of division, some of the metal passes over into the distillate. The easiest way is to filter the distillate, and, after washing the filter paper with water, alcohol, and ether, to examine it with a magnifying glass.

L. DE K.

Titration of Mercuric Chloride and "Sublimate Pastilles." ERWIN RUPP (*Chem. Zentr.*, 1910, **1**, 478; from *Apoth. Zeit.*, 1909, **24**, 939).—Ten to fifty c.c. of the neutral solution containing 1—5% of mercuric chloride are mixed with 5—10 drops of 1% phenolphthalein and titrated with *N*/2-potassium cyanide. If the original solution is acid towards litmus paper on adding sodium chloride, one drop of phenolphthalein is added first and then *N*/10-alkali until neutral; more phenolphthalein is then added, and the titration continued with pure potassium cyanide.

In the case of pastilles, five or ten (weighing respectively 1 gram or 0·5 gram each) are dissolved in water, and the solution is diluted to 250 c.c. 0·1—0·2 Gram of purified animal charcoal is added, and, after shaking for two minutes, the liquid is filtered; 50 c.c. of the decolorised solution are then titrated with cyanide. Two mols. of potassium cyanide = one mol. of mercuric chloride.

L. DE K.

Volumetric Estimation of Aluminium Salts. LUCIEN TELLE (*Chem. Zentr.*, 1910, i, 382; from *Bull. Sci. Pharm.*, 1909, **16**, 656—658).—Ten c.c. of approximately 2% alum solution (free from ammonia) are diluted with 40 c.c. of water, heated to boiling, and titrated with *N*/10-barium hydroxide, using phenolphthalein as indicator; this gives the free and combined acid. 0·5—1 Gram of pure potassium fluoride is dissolved in a silver or nickel dish in 50 c.c. of water, heated to boiling, and neutralised; 10 c.c. of the alum solution are added, and the solution is again neutralised with *N*/10-barium hydroxide at the boiling heat. This gives the amount of free acidity, and the difference represents the combined acidity, which in turn represents the aluminium.

In presence of iron, the alumina is first separated by means of sodium thiosulphate, and then introduced into a boiling 2% solution of neutral potassium fluoride. A definite volume of *N*/10-sulphuric acid is added, and, after boiling a few minutes, the excess of acid is titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator.

L. DE K.

Rational Analysis of Clays. WALTER C. HANCOCK (*J. Soc. Chem. Ind.*, 1910, **29**, 309—311).—The process given in Lunge's "Methods of Technical Analysis" is recommended.

The potassium present may be taken as representing approximately felspar, whilst the clay substance may be calculated either from the amount of combined water or from the aluminium less that required for the felspar. Quartz remains undissolved after heating with sulphuric acid, and may be freed from admixed silica by warming with 5% solution of sodium hydroxide, or, according to Koerner, by warming for five minutes on the water-bath with 0·5% hydrofluoric acid.

L. DE K.

Titration of Ferrous Salts in the Presence of Hydrochloric and Phosphoric Acids. GEORGE J. HOUGH (*J. Amer. Chem. Soc.*, 1910, **32**, 539—540).—Solutions of ferrous salts containing hydrochloric acid can be accurately titrated with potassium permanganate if phosphoric acid is previously added to the solution. The method is recommended for the estimation of iron in iron ores, and is said to give excellent results, provided that as little hydrochloric acid as possible (not exceeding 5—10 c.c. of the concentrated acid) is used, that the titration is carried out in a cold solution of about 300 c.c. volume, and that stannous chloride is not employed to reduce the iron.

E. G.

Estimation of Ferric Iron in the Presence of Ferrous Iron. W. SCHATZ (*Pharm. Zeit.*, 1910, **55**, 292).—The author confirms the statement of Joseph (this vol., ii, 351) that in Mohr's method of estimating ferric iron (liberation of iodine from potassium iodide) there is no need to operate in an atmosphere of carbon dioxide.

The process is also applicable in the presence of ferrous iron. The author uses starch as indicator, and titrates with *N*/10-thiosulphate rapidly until perfectly colourless; no inconvenience is then experienced from a return of the blue colour. L. DE K

Analysis of Pyrites. Wilhelm Vilstrup (*Chem. Zeit.*, 1910, **34**, 350—351).—The sulphur and iron are estimated by Lunge's method. The other constituents are estimated as follows: 12·5 grams of the powdered ore are moistened in a large beaker with 10 c.c. of water and 1 c.c. of sulphuric acid, and strong nitric acid is added until there is no further effervescence. The liquid is now boiled down to a paste, and the residue treated with boiling water. If the residue is not white, the liquid is decanted, and the insoluble mass boiled with *aqua regia*. This is then evaporated and the residue transferred to the main solution, and the whole diluted to 250 c.c. The solution is then passed through a dry filter; the residue is washed, and then tested for lead by boiling with ammonium acetate; excess of sulphuric acid reprecipitates the lead. Two hundred c.c. of the filtrate (10 grams of sample) are treated with hydrogen sulphide. The precipitate, consisting of copper and arsenious sulphides, is digested with ammonium carbonate; this dissolves the arsenic, which is then reprecipitated by adding dilute sulphuric acid and passing hydrogen sulphide. The arsenious sulphide is collected in a Gooch crucible, washed with alcohol and carbon disulphide, dried at 100°, and weighed. The copper sulphide is freed from admixed sulphur and traces of antimony sulphide by boiling with sodium sulphide, and then washed and burnt to oxide. The filtrate from the copper–arsenic precipitate is diluted to 500 c.c. Fifty c.c. (1 gram sample) are boiled, oxidised with nitric acid, and, after adding an excess of ammonium chloride, precipitated with ammonia. As the iron precipitate retains zinc it should, after washing, be redissolved in hydrochloric acid, and, after neutralisation, boiled with ammonium acetate or nitrite. The united filtrates then contain all the zinc. After adding excess of ammonia and heating to boiling, any calcium and magnesium are precipitated by adding a little ammonium carbonate and phosphate; the liquid should then be stirred for half an hour. From the filtrate, the zinc ammonium phosphate is recovered by boiling off the ammonia, and finally converted by ignition into zinc pyrophosphate and weighed as such. If the colour should not be pure white, traces of nickel or cobalt phosphate may be present. In such cases, the filtrate from the iron is acidified with acetic acid and treated with hydrogen sulphide. After twenty-four hours, the precipitate is collected and treated with cold *N*-hydrochloric acid, the zinc dissolves, and the nickel and cobalt are not affected. From the filtrate, the zinc is then recovered as pyrophosphate as usual. L. de K.

Direct Titrations of Cobalt and Nickel. Erwin Rupp and F. Pfenning (*Chem. Zeit.*, 1910, **34**, 322—323).—*Cobalt.*—Five to ten to 25 c.c. of *N*/2-potassium cyanide are taken, and the cobalt sulphate solution (containing 0·2—0·75% of metal and free from acidity) is added until a faint permanent turbidity is formed. One c.c. of *N*/2-cyanide = 0·0059 gram of cobalt.

Nickel.—The process for cobalt may be also used for nickel, but it is advisable to add 5 to 20 drops of 10% ammonia; too large an excess of ammonia is, however, injurious. 1 c.c. of *N*/2-cyanide = 0·0073375 gram of nickel.

The reverse process is, however, more convenient. A measured volume of the neutral nickel solution is mixed with 10 drops of 1% phenolphthalein, and titrated with $N/2$-potassium cyanide until the liquid gets clear and has a decidedly red colour. A third plan is to add to the neutral nickel solution a definite volume of $N/2$-cyanide, and then to titrate the excess with $N/2$-acid, with methyl-orange as indicator.

These last two methods are not applicable in the estimation of cobalt. L. DE K.

The Rapid Electrolytic Precipitation of Tin. B. PASZTOR (*Elektrochem. Zeitsch.*, 1910, **16**, 281).—An account of experiments on the electrolytic precipitation of tin with varying strengths of current at different temperatures and in various solvents. The material employed was the double ammonium stannichloride, $SnCl_4,2NH_4Cl$, whilst tartaric, formic, and oxalic acids were found to be suitable electrolytes. The results are tabulated, and the character of the precipitates obtained is described. F. M. G. M

Estimation of Thorium in Monazite Sand. RICHARD J. MEYER and M. SPETER (*Chem. Zeit.*, 1910, **34**, 306—308).—Fifty grams of the sample are heated with 100 c.c. of strong sulphuric acid for six hours at 250°, and, when cold, 500 c.c. of cold water are added. The solution is filtered and, when cold, diluted to 1 litre, and 100 c.c. are then taken for analysis. After adding 50 c.c. of nitric acid, D 1·4, and cooling, a cold solution of 15 grams of potassium iodate in 50 c.c. of nitric acid and 30 c.c. of water is added, and, after half an hour, the thorium iodate is collected and washed with a solution containing 2 grams of potassium iodate in 50 c.c. of dilute nitric acid and 200 c.c. of water. The precipitate is returned to the beaker, and again stirred and washed. It is now again transferred to the beaker by means of a jet of hot water, heated to boiling, and dissolved in 30 c.c. of strong nitric acid; addition of 4 grams of potassium iodate dissolved in hot water causes it to reprecipitate. The precipitate is now collected on the same filter and washed as before, and is then quite free from cerium. It is dissolved in hydrochloric acid with the aid of sulphur dioxide, and precipitated with ammonia at the boiling heat. The hydroxide is washed with boiling water, redissolved in dilute hydrochloric acid, and precipitated with excess of oxalic acid. The precipitate is washed with water, acidified with hydrochloric acid, and then ignited to oxide. L. DE K.

Estimation and Separation of Palladium. ALEXANDER GUTBIER and FERDINAND FALCO (*Zeitsch. anal. Chem.*, 1910, **49**, 287—295).—About 0·2 gram of the palladium halogen salt is dissolved in a little very dilute hydrochloric or hydrobromic acid, diluted to 150 c.c., and heated to boiling, when a boiling aqueous solution of hydrazine sulphate is added. The beaker is now placed on a boiling water-bath until the metal has separated completely, and the excess of the reagent is then destroyed by half an hour's active boiling. The palladium is collected on a filter, washed, and dried at 115°. It is then detached from the filter, which is burnt separately in a porcelain boat,

and, after adding it to the ash, the whole is ignited, first in a current of air, then in a current of hydrogen, and finally in a current of carbon dioxide free from oxygen. The reduction may be also effected in ammoniacal solution. In the filtrate the halogen may be estimated by means of silver nitrate as usual. L. DE K.

Moist Combustions with Caro's Acid. WILHELM MIGAULT (*Chem. Zeit.*, 1910, **34**, 337).—The acid is prepared by adding slowly 3—4 volumes of sulphuric acid to 1 vol. of 30% hydrogen peroxide (perhydrol), and is a most powerful oxidiser. In practice, to each gram of the organic substance to be destroyed is added 2—4 c.c. of perhydrol and then 6—12 c.c. of sulphuric acid. The whole is then heated at 100°, and towards the end at 140°. If necessary, the solution is allowed to cool and then again warmed with some more perhydrol. L. DE K.

Elementary Analysis by means of a Calorimetric Bomb. HAROLD L. HIGGINS and ALICE JOHNSON (*J. Amer. Chem. Soc.*, 1910, **32**, 547—558).—A method is described for the simultaneous estimation of carbon and hydrogen and the determination of the heat of combustion by means of the calorimetric bomb, and is recommended especially for the analysis of food, fæces, and urine. A description is given of the apparatus employed, the method of manipulation, and the mode of calculating the results. The carbon can be estimated with a maximum error of ± 0·7% of the amount present, and the hydrogen with an error of between 2% and 6%. E. G.

The Technique of Carbon Dioxide Estimation by means of the Berthelot Bomb. E. GRAFE (*Biochem. Zeitsch.*, 1910, **24**, 277—281).—The carbon can be estimated in a substance at the same time as the calorimetric value. Two valves must be supplied to the bomb, one for the outlet of the carbon dioxide, after combustion of the substance in oxygen, and the other for the inlet of dry carbon dioxide-free air, for driving out the last traces of the gas after the pressure in the bomb has reached the atmospheric pressure.

In the case of nitrogenous and sulphur-containing substances, small quantities of water should be added before combustion to keep back the nitric and sulphuric acids. S. B. S.

Estimation of Petroleum Derivatives and Resins in Turpentine Oils. PAUL NICOLARDOT and LOUIS CLÉMENT (*Bull. Soc. chim.*, 1910, [iv], **7**, 173—176).—Fifty c.c. of turpentine oil are dissolved in 50 c.c. of glacial acetic acid in a reflux apparatus; nitric acid (D 1·2) is added drop by drop during an hour, or until nitrous fumes appear. The mixture is distilled in steam, and the volatile petroleum derivatives dried over potassium carbonate and measured. The process is less dangerous than the usual method, and gives better results. The resins are estimated by washing the non-volatile magma, extracting with chloroform, and weighing after removal of the solvent by evaporation.

Details are also given for the analysis of turpentine oils by oxidation with chromic acid and mercuric acetate. W. O. W.

Analysis of Turpentine Oil by Miscibility Curves. MAURICE VÈZES (*Compt. rend.*, 1910, **150**, 698—700).—The conclusions of Louise (this vol., ii, 357) have been confirmed by experiments on the reciprocal solubility of aniline and turpentine, but the miscibility curves obtained are of somewhat different shape to those shown by this author. This is explained by the marked effect produced by acidity, especially when this is due to resin. Before applying the method to commercial turpentine oils, the samples should be distilled and the neutrality of the fractions assured. W. O. W.

Detection of Methyl Alcohol in General, and Especially in Presence of Ethyl Alcohol. GEORGES DENIGÈS (*Compt. rend.*, 1910, **150**, 832—834. Compare this vol., ii, 357).—The following method is given for detecting traces of methyl alcohol in ethyl alcohol: 0·1 c.c. of alcohol is mixed with 5 c.c. of a 1% potassium permanganate solution and 0·2 c.c. of pure sulphuric acid. After three minutes, 1 c.c. of a cold saturated solution of oxalic acid is added. When the liquid has become pale yellow, it is shaken with 1 c.c. of pure sulphuric acid. The colourless liquid is then treated with 5 c.c of Schiff's reagent, prepared as described previously. The appearance of a violet colour after some minutes indicates the presence of methyl alcohol. This process will detect one part of methyl alcohol in 1000 parts of ethyl alcohol, but if the liquid is submitted to fractionation, one part in 10,000 may be detected.

The presence of ethyl alcohol is advantageous, as it admits of the transient formation of an acetal, which readily reacts with Schiff's reagent. When methyl alcohol is sought for in aqueous solution, the process is modified as follows: 3 c.c. of the solution (containing less than 4% of methyl alcohol) are mixed with 1 c.c. of pure ethyl alcohol and 2 c.c. of potassium permanganate solution (2·5%). The mixture is shaken with 2 c.c. of sulphuric acid, and the process completed as before. Under these conditions, a few mg. of methyl alcohol may be detected in 100 c.c. of water. W. O. W.

Toxicological Detection of Alcohol. MARCO T. LECCO (*Zeitsch. anal. Chem.*, 1910, **49**, 285).—On evaporating a distillate to be tested for phosphorus with nitric acid on the water-bath, the author noticed the formation of oxalic acid crystals, and further investigation showed that this was caused by the presence of alcohol in the intestines analysed. The other volatile organic matters present do not yield the crystals. L. DE K.

Estimation of Dry Extract in Wines. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1910, **15**, 135—137).—The wine is concentrated by distillation or evaporation to exactly one-third of its volume, and when cooled to between 20 and 30° its sp. gr. is taken with a delicate hydrometer. For every 5° over 15°, a correction should be made of +0·002.

The figure over 1·0000 is then multiplied with a factor varying from 0·21 to 0·26 (see Blarez's table in the original paper), and the result is divided by the empirical factor 2·87. L. DE K.

A Reaction of Amyl Alcohol. H. VON WYSS, E. HERZFELD, and O. REWIDZOFF (*Zeitsch. physiol. Chem.*, 1910, **64**, 479—480).—Normal urine gives an intense blue coloration with four drops each of solutions 1, 2, and 3 and 10 drops of solution 4; (1) contains 4·5 grams of α-naphthol in 100 c.c. of cold 50% alcohol; (2) 4·5 grams of *p*-phenylenediamine in 100 c.c. of absolute alcohol; (3) 4·5 grams of sodium carbonate (anhyd.) in 100 c.c. of water; (4) 3% hydrogen peroxide solution.

Amyl alcohol (2 c.c.) also gives an intense blue coloration with a mixture of four drops of each of the solutions 1, 2, and 3. *iso*Butyl alcohol also gives a coloration, but not so intense, and heptyl, ethyl, and cetyl alcohols, glycerol and wax give feeble colorations. Methyl and propyl alcohols, sucrose, inositol, methyl and ethyl acetates, acetone, light petroleum, benzene hydrocarbons, chloroform, fatty acids, purine bases, creatine, &c., do not give a coloration.

J. J. S.

Estimation of Cholesterol and Cholesterol Esters in some Normal and Pathological Kidneys. ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1910, **65**, 110—117).—The kidneys are comminuted and mixed with three times the bulk of anhydrous gypsum, and, after the mass has hardened, it is reduced to fine powder and then extracted in a large Soxhlet apparatus for three to five days with ether or light petroleum. The solution is evaporated, and the residue dissolved in thirty times its weight of hot 95% alcohol. (If any residue should remain, this may retain cholesterol ester; it should be dissolved in ether-alcohol and added to the filtrate of the digitonin precipitate.) To this is then added a 1% alcoholic solution of digitonin in slight excess. After a few hours, the precipitate is collected on a Gooch filter, washed with alcohol and ether, dried at 100°, and weighed; it contains 25% of cholesterol.

The filtrate is concentrated, and, after adding some water, shaken with light petroleum (or ether). The excess of digitonin remains in the weak alcoholic liquid, whilst the cholesterol, fatty matters, and other lipoids pass into the upper layer. The solvent is then distilled off, and the residue saponified with hot alcoholic sodium ethoxide. The liberated cholesterol is extracted with light petroleum, and finally weighed as the digitonin compound.

On applying the process to normal and to diseased kidneys, the author noticed, in the case of the latter, an enormous increase in the amount of the cholesterol esters; the free cholesterol, however, showed no great differences.

L. DE K.

Precipitation of Reducing Sugar by Lead Acetate and the Estimation of Reducing Sugars. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 856—860).—It is pointed out that clarification of crude sugars, molasses, etc., with lead acetate causes a part of the reducing sugars present to be precipitated, and that, in order to ascertain the actual quantity of these sugars, the estimation of the same should be carried out on a solution of the sample which has not been subjected to any other treatment than filtration. W. P. S.

Estimation of Dextrose in Blood. Berthold Oppler (*Zeitsch. physiol. Chem.*, 1910, **64**, 393—422).—The following method is finally recommended: The blood collected in ammonium oxalate is diluted with water, and precipitated in the dark with a 10% solution of phosphotungstic acid. The filtrate is freed from the excess of the reagent by means of lead acetate, the excess of which is then, in turn, removed by hydrogen sulphide. The filtrate, after being duly concentrated, may then be examined polarimetrically, or the dextrose may be estimated by the fermentation process or by one of the reduction methods; in this case, Bertrand's process (Abstr., 1907, ii, 136) is recommended.

L. de K.

Bromine Water as an Agent for Discriminating between Aldoses and Ketoses. Emil Votoček and J. Němeček (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 399—402).—The authors have already made a physico-chemical study of the reaction between aldoses and bromine water (this vol., i, 95). Experiments showed that ketoses were not acted on at the ordinary temperature, and the object of the present investigation was to ascertain the conditions of concentration and temperature under which the maximum oxidation of aldoses should occur, the ketoses not being attacked. Both at 100° and at 60° some of the ketose (fructose) was oxidised, but not at 21°.

The following method is recommended: 0·5 gram of the pure sugar, the nature of which is to be discovered, is dissolved in less than 10 c.c. of water, 40 c.c. of bromine water (saturated at the ordinary temperature) are added, and the whole made up to 50 c.c. with water. After twenty-four hours at 21°, the sugar remaining in 25 c.c. of the solution is determined by Allihn's method. *d*-Galactose and *l*-arabinose are almost completely oxidised. Dextrose and *l*-xylose oxidise to the extent of 78 and 74% respectively, and rhamnose to the extent of 61%. *d*-Fructose, on the other hand, is not acted on. E. J. R.

The Influence of Optically Active Non-sugar Material on the Estimation of Sugar in the Sugar Beet. Karl Andrlík and Vl. Staněk (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 385—399).—When the extract of sugar beets, obtained in the usual hot-water digestion and lead acetate method, is concentrated by evaporation to about one-fifth of its volume, there is a decrease in the amount of polarisation effected amounting to about 0·2°. The cause of this phenomenon was not ascertained. The value is, however, higher by about 0·11% than corresponds with the amount of sucrose as determined by Clerget's method; it therefore appears that other optically active substances besides sugar are present in the extract, notwithstanding the clearing action of the lead acetate. The active substances are not the raffinose and amino-acids already known.

The expressed juice and the solution obtained by the diffusion process contain the same substances. In normal cases, however, their amount is only small. E. J. R.

Detection of Sucrose in Wine, Pale Ale, etc. S. Rothenfusser (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 261—268).—The test described

depends on the blue coloration which is produced when sucrose is heated with diphenylamine in the presence of hydrochloric and acetic acids, and also on the fact that other substances, such as dextrin, invert sugar, maltose, organic acids, etc., which would interfere with the reaction, may be removed by precipitation with ammoniacal lead acetate solution. In the case of wine, a small quantity of the sample is neutralised, and to 20 c.c. of the solution are added 10 c.c. of slightly ammoniacal 5% casein solution, 4 c.c. of normal lead acetate solution (prepared by dissolving 500 grams of lead acetate in 1200 c.c. of water), and 2 c.c. of ammonia, D 0·944. The mixture is shaken, and, after the lapse of ten minutes, is poured on a filter. Three c.c. of the filtrate are then heated in a test-tube in a boiling water-bath for ten minutes with 3 c.c. of diphenylamine solution; the latter is prepared by mixing 10 c.c. of a 10% alcoholic diphenylamine solution with 25 c.c. of glacial acetic acid and 65 c.c. of hydrochloric acid, D 1·19. A blue coloration is produced if as little as 0·01% of sucrose is present. If the wine contains more than 3·0% of invert sugar, it is necessary to increase the proportion of casein and lead acetate solutions with which the wine is treated in order that all invert sugar may be precipitated. To see whether all this sugar has been removed, 5 c.c. of the filtrate should be tested with Fehling's solution in the usual way; when the filtrate from a wine yields a blue coloration with the diphenylamine reagent, but gives no reduction with Fehling's solution, it may be safely concluded that sucrose is present. Sweet wines and pale ale should be diluted with from 1 to 7 parts of water before being tested. The reaction may also be employed for the detection of sucrose in lactose and in fruit juices; orange juice gives an intense coloration when treated as described, but does not reduce Fehling's solution. W. P. S.

Estimation of Cellulose by the Methods of Lange and of Simon and Lohrisch. ARTHUR SCHEUNERT and ERNST LOTSCH (*Zeitsch. physiol. Chem.*, 1910, **65**, 219—231).—Simon and Lohrisch's method is not accurate, for treatment with concentrated potassium hydroxide alters cellulose considerably. The older method of Lange is also unsuitable for quantitative purposes, for treatment with hydrogen peroxide in concentrated alkaline solution destroys the cellulose. W. D. H.

The Action of Fats on Osmium Peroxide. L. GOLODETZ (*Chem. Rev. Fett. Harz. Ind.*, 1910, **17**, 72—73).—The black colour which is produced when fats are mixed with osmium peroxide is due to the reduction of the latter, a lower oxide or metallic osmium being formed. The reduction is caused by the oleic acid or olein present in the fats; oleic acid which has been saturated with bromine does not reduce osmium peroxide, and the reaction depends, therefore, on the unsaturated state of the oleic acid. W. P. S.

Determination of the Saponification Number of Dark-coloured Oils. OTTO SCHUTTE (*Chem. Zeit.*, 1910, **34**, 351. Compare Marx, this vol., ii, 360; Mayer, this vol., ii, 361).—The author uses,

successfully, the following process for the estimation of fatty oils in presence of much dark-coloured mineral oils (cylinder oils).

Five to fifteen grams of the sample are dissolved in 25 c.c. of pure benzene, 25 c.c. of *N*/2-alcoholic sodium hydroxide are added, and the whole boiled in a reflux apparatus for an hour. The excess of alkali is then at once titrated with *N*/4-sulphuric acid, using "alkali-blue" as indicator. As soon as the bulk of the alkali has been neutralised, 30 c.c. of chloroform are added, which carries down with it the benzene layer; the change from red to pure blue is then readily noticed. A blank experiment should be made. The sodium hydroxide absorbed serves to calculate the amount of fatty matter. L. DE K.

Detection of Formaldehyde in Wines. A. HUBERT (*Ann. Chim. anal.*, 1910, **15**, 100—103).—An adverse criticism of the method recommended by Rouillard and Goujon (this vol., ii, 239) for the detection of the formaldehyde derived from urotropine (hexamethylenetetramine) used for desulphitation of wines. If, in presence of urotropine, sulphur dioxide is estimated by Rippert's method, there is a serious deficit, but if Haas's process is employed, nearly the whole of it is recovered; the sulphur dioxide, however, must have been added recently.

If in a wine of great alcoholic strength but a very small amount of sulphur dioxide is found, it is certain that some preservative, such as formalin or urotropine, has been added in addition. Formaldehyde may often be recognised by its odour when the wine is heated with a little calcium peroxide to oxidise the sulphites. For its estimation, 100 c.c. of wine are acidified with 5 c.c. of phosphoric acid, D 1·3, and distilled until 30 c.c. have been collected. The distillate is then titrated by Legler's well-known ammonia process as modified by Schaffer. L. DE K.

Estimation of Formaldehyde in Formalin Soaps (Lysoform, Formosapol, and Morbizid). O. ALLEMANN (*Zeitsch. anal. Chem.*, 1910, **49**, 265—269).—Fifty c.c. of the formalin soap solution are diluted with 250 c.c. of water, barium chloride is added as long as a precipitate forms, and the whole is diluted to 500 c.c.; in the case of "Morbizid" it is diluted to a litre. Five c.c. of the filtrate are mixed with 40 c.c. *N*/10-iodine, and aqueous sodium hydroxide is added until the colour changes to bright yellow. After ten minutes, the liquid is acidified with sulphuric or hydrochloric acid, and the excess of iodine titrated with *N*/10-sodium thiosulphate (Romyn's method).
L. DE K.

Detection of Acetone. LEOPOLD ROSENTHALER (*Zeitsch. anal. Chem.*, 1910, **49**, 299).—A question of priority. The author noticed the same colorations (*ibid.*, 1909, **48**, 165) as described by Fritsch (this vol., ii, 165). L. DE K.

Iodometric Estimation of Acetone. LUDWIG KRAUSS (*Chem. Zentr.*, 1910, i, 767; from *Apoth. Zeit.*, 1910, **25**, 22).—The estimation of acetone in urine is generally carried out by the Messinger-Huppert process, but the results are not always concordant. If, however, the

mixture of acetone solution, *N*-alkali, and *N*/10-iodine solution is frequently shaken for a quarter of an hour and then acidified with 5% hydrochloric acid, the iodine separated may be titrated accurately.

The distillate of a urine free from acetone was used for test experiments, and the acetone added was entirely recovered.

L. DE K.

Detection of Hexamethylenetetramine in Wine. BONIS (*Ann. Falsif.*, 1910, **3**, 106—112).—The magenta-sulphurous acid test recommended by Rouillard and Goujon (this vol., ii, 239) is trustworthy provided that the distillate or wine is acidified with one-fifth of its volume of sulphuric acid before the reagent is added. Under these conditions the test is characteristic of formaldehyde; acetaldehyde does not yield a coloration. As regards the question whether the detection of formaldehyde in a wine is an indication that the latter has been treated with hexamethylenetetramine, the author is of opinion that it is necessary to detect the presence of an undue quantity of ammonia in a wine, in addition to formaldehyde, before an affirmative answer can be given. As wine which has received the addition of a definite quantity of hexamethylenetetramine does not yield a quantity of ammonia corresponding with that equivalent to the amount formed by the decomposition of the hexamethylenetetramine, it is impossible to estimate the quantity of the latter substance present from the ammonia content of a wine. By comparing the result obtained on the analysis of a sample with those yielded by samples of wine containing known quantities of hexamethylenetetramine, the approximate amount of the latter may, however, be obtained.

W. P. S.

Detection of Hexamethylenetetramine in Musts and Wines. E. VOISÉNET (*Compt. rend.*, 1910, **150**, 879, 882).—Details are given for the detection of hexamethylenetetramine in wines by taking advantage of the production of a violet coloration when albumin is treated with hydrochloric acid in presence of nitrous acid and formaldehyde (Abstr., 1905, ii, 59). Twenty-five c.c. of the wine are distilled with two drops of sulphuric acid, and the test applied to the distillate, after rejecting the first 5 c.c. (or 10 c.c. in the case of wines containing much sugar).

W. O. W.

Estimation of Amino-acids, Polypeptides, and Hippuric Acid by means of the Formaldehyde Titration. VALDEMAR HENRIQUES and SÖREN P. L. SÖRENSEN (*Zeitsch. physiol. Chem.*, 1910, **64**, 120—143. Compare this vol., ii, 164).—A slight modification of the method used previously, owing to the observation made by de Jager that ammonium compounds interfere with the process.

Estimation of ammonia and amino-acids.—Fifty c.c. of urine are treated with phenolphthalein, barium chloride, and barium hydroxide and diluted to 100 c.c. Eighty c.c. of the filtrate are distilled in a vacuum, and the ammonia is titrated as usual. The residue in the flask is dissolved in a few c.c. of hot *N*-hydrochloric acid, and a current of air free from carbon dioxide is passed. The solution is then transferred to a 100 c.c. flask, and, after neutralising with *N*-sodium

hydroxide, using litmus paper as indicator, it is diluted to the mark with water free from carbon dioxide. Forty c.c. of the liquid are then titrated for amino-acids by means of formaldehyde.

Estimation of Hippuric acid and Peptide-combined Nitrogen.—Fifty c.c. of the urine are acidified with 5 c.c. of 5*N*-hydrochloric acid, and shaken six times in succession with ethyl acetate to extract the hippuric acid. This is then converted, by boiling the residue left on evaporation with 50 c.c. of 30% hydrochloric acid, into benzoic acid and glycine. The latter may then be estimated, after removing the excess of acid by evaporation, by the formaldehyde method.

The urine free from hippuric acid is boiled for three hours in a long-necked flask with 50 c.c. of hydrochloric acid, and then concentrated on the water-bath. The residue is mixed with 1 c.c. of phenolphthalein solution, neutralised with sodium hydroxide, and, after adding 2 grams of barium chloride, diluted to 50 c.c. with saturated solution of barium hydroxide. Forty c.c. of the filtrate are acidified with hydrochloric acid, an extra 5 c.c. of *N*-acid are added, and then 20 c.c. of *N*/3-silver nitrate to decolorise the solution. After diluting to 100 c.c., 80 c.c. of the filtrate are treated as before, the ammonia is expelled with barium hydroxide, and the residue titrated as directed by means of formaldehyde; the result equals peptide-combined nitrogen.

Normal urine, whether from man or animals, always contains peptide-combined nitrogen as a regular constituent. L. DE K.

The Formaldehyde Titration [of Amino-acids, etc.] in Urines. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, **65**, 185—188. Compare Henriques and Sörensen, preceding abstract).—As Sörensen's process is more simple, and as the red colour with phenolphthalein is more easily controlled than the test with litmus paper, the author prefers this method in the case of amino-acids (also compare Malfatti, Abstr., 1909, ii, 837). L. DE K.

A New Reaction of Urine. HEINRICH SCHUR (*Chem. Zentr.*, 1910, i, 63; from *Wien. Klin. Woch.*, 1909, **22**, 1587—1588).—The very delicate iodine test for adrenaline (red coloration) is often given by pure urines. The colour soon fades even if adrenaline has been purposely added. The active principle is not removed by shaking the urine with ether. L. DE K.

Colorimetric Estimation of Adrenaline. A. ZANFROGNINI (*Chem. Zentr.*, 1909, ii, 2205—2206; *Deut. med. Woch.*, 1909, **35**, 1752—1753).—The test is based on the fact that an emulsion of manganese peroxide is reduced by adrenaline, and yields a rose-coloured solution; any excess of the peroxide may be removed by hydrogen peroxide. The reagent is prepared by adding eight drops of lactic acid to a solution of 3 grams of potassium permanganate in 24 c.c. of water.

The adrenaline is recovered from the kidneys by rubbing with sand to a fine powder and extracting with ten parts of 0.2% acetic acid, with addition of a little thymol, and heating for fifteen minutes on the water-bath at 70°. The residue is then washed with five parts of

the same acid, and the filtrate is decolorised by addition of a sufficiency of ammonium sulphate.

Ten c.c. of standard adrenaline (one per million) are mixed with one drop of the reagent, and, after five minutes, a drop of hydrogen peroxide is added. The liquid to be tested is then diluted repeatedly, until at last 10 c.c. give the same reaction as the standard solution.

L. DE K.

Accurate Method for the Estimation of Caffeine in Tea and Green or Roasted Coffee. JAMES BURMANN (*Bull. Soc. chim.*, 1910, [iv], 7, 239—244).—After pointing out certain sources of error in Keller's method for the analysis of tea and coffee, the author describes a process whereby the caffeine is separated by sublimation. The apparatus employed consists of a test-tube (15—18 cms. long, 15—18 mm. diam.) having a constriction near each end. The lower constriction is plugged with asbestos, and the mouth of the tube closed by cotton wool. The tube is immersed up to the first constriction in a bath of paraffin. Five grams of the finely-divided material are dried and extracted with light petroleum to determine the fat. The residue is shaken with 150 grams of chloroform, treated with 5 grams of a 10% ammonia solution, and again shaken for half an hour. After filtration, the chloroform is removed and the crude caffeine weighed. This is again dissolved in chloroform and introduced into the special tube. After removal of the solvent at 100°, the tube is heated at 210—240° for three hours and then cut at the constriction. The caffeine, which is sufficiently pure for ordinary analyses, is removed by chloroform and weighed. A second sublimation gives perfectly pure caffeine, m. p. 234°.

W. O. W.

The Behaviour of Proteins to Acetone. THEODOR WEYL (*Zeitsch. physiol. Chem.*, 1910, **65**, 246—250. Compare this vol., i, 287).—Acetone is a useful reagent for the quantitative precipitation of many proteins. In human milk, the precipitate may be first freed from fats and then weighed, or the nitrogen in the precipitate may be estimated by Kjeldahl's method. In three specimens of human milk, 100 c.c. contained 1·15, 0·7, and 0·6 gram of total protein; the yield of caseinogen by Hammarsten's method is less in each case; the difference represents lactalbumin. Various amino-acids and polypeptides, dextrose, lactose, and creatinine are also precipitable by acetone. The precipitation of amino-acids is regarded as explaining the precipitability of proteins.

W. D. H.

The So-called Cammidge Pancreas Reaction. OTTO SCHUMM, C. HEGLER, and Mdme. MEYER-WEDELL (*Chem. Zentr.*, 1909, ii, 2205; from *Münch. med. Woch.*, 1909, **56**, 1878—1880).—The "Cammidge reaction" has been applied by the authors to a large number of urines, and found to be untrustworthy (compare also this vol., Abstr., ii, 163).

L. DE K.

General and Physical Chemistry.

Variation of the Emissive Power of Metals with the Temperature in the Short-waved Ultra-red Spectrum. E. HAGEN and HEINRICH RUBENS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 467—487. Compare Abstr., 1909, ii, 358).—It has been shown previously that the emissive power of metals for ultra-red rays of long wave-length ($\lambda = 26{\cdot}0\mu$ and $\lambda = 8{\cdot}85\mu$) varies with the temperature, as required by Maxwell's theory. For visible rays the variation is small, and the authors have now made measurements in the intervening region, using the residual rays obtained by reflexion from calc-spar ($\lambda = 6{\cdot}65\mu$) and rays ranging from $\lambda = 5{\cdot}0\mu$ to $0{\cdot}78\mu$ obtained by means of a spectrometer. For temperatures ranging from 100° to 500° and rays of wave-length $\lambda = 6\ 65\mu$, all the metals examined (silver, gold, platinum, nickel, brass, platinum-silver, constantan, and nickel-steel) exhibit variations of emissive capacity, the magnitude of which is that required by the electro-magnetic theory. For rays of shorter wave-length than $\lambda = 2\mu$, the temperature variation observed in the case of nickel, constantan, mirror-metal, and unhardened steel. is very small. It increases as the wave-length increases from $\lambda = 2\mu$ to $\lambda = 5\mu$, and for rays of the latter wave-length the temperature variation has attained the magnitude anticipated by Maxwell's theory.

H. M. D.

Special Type of Discontinuous Emission Spectra of Solid Substances. EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1910, **12**, 376—384. Compare Abstr., 1904, ii, 689, 690).—Further observations relating to the emission spectra exhibited by solid substances under the influence of cathode rays are recorded. For one and the same substance three different spectra can be obtained, and these are distinguished as the preliminary, chief, and solution spectra. The intensity of the preliminary spectrum is greatest when the substance is first acted on by the cathode rays. The discontinuous preliminary spectra of benzene derivatives are in very many cases of the same type, and show six groups of similarly constituted bands. The intensity and persistence of these spectra are greatly increased by the addition of very small quantities of aldehydes or ketones containing the benzene carbon ring. Similar spectra containing six groups of bands are obtained on the addition of very small quantities of these aldehydes or ketones to aliphatic compounds. It is supposed that the appearance of the spectra is connected with the general tendency of the aldehydes and ketones to undergo polymerisation. The less intense spectra of the same type which are obtained when the pure hydrocarbons and certain of their substitution products are subjected to cathode rays are considered to indicate that these substances also undergo polymerisation to a very small extent, this process being favoured by a lowering of the temperature.

H. M. D

Absorption Spectra. I. Saturated Iodine Compounds. CECIL REGINALD CRYMBLE, ALFRED WALTER STEWART, and ROBERT WRIGHT (*Ber.*, 1910, **43**, 1183—1187).—The authors propose to make a comparison of the spectra of iodine compounds with the object of arriving at results applicable to the explanation of substitution in general. The spectra of methyl iodide, ethyl iodide, *iso*butyl iodide, and *iso*amyl iodide all show a band of which the maximum lies about the frequency 3900. This the authors considers to be characteristic of the system $R·CH_2I$. Ethylene iodide shows the same band, but more strongly. Methylene iodide has a band with its maximum at 3300, and this the authors ascribe to the presence of two neighbouring iodine atoms. In agreement with this theory, they find the same band in the spectra of iodine, iodoform, and potassium tri-iodide. In the last two a band with maximum 2800 is also present, and this is connected with the presence of three iodine atoms in the molecule. A band with maximum about 2100 occurs in the spectrum of iodine: concerning this no hypothesis is suggested. R. V. S.

Absorption Spectra. II. The Colour of Azobenzene. CECIL R. CRYMBLE, ALFRED W. STEWART, and ROBERT WRIGHT (*Ber.*, 1910, **43**, 1188—1191).—From a comparison of the spectra of azobenzene and stilbene, the authors consider that the isorropesis hypothesis of Baly and Tuck (Trans., 1906, **89**, 982) does not suffice to explain the colour of azobenzene, for, although in stilbene all the conditions are fulfilled which that theory requires, yet it has no band in the visible spectrum. Moreover, the group $-N:N-$ may give a coloured compound where no possibility of isorropesis is present, as in diazomethane. Attention is called to an error in the curve for stilbene in a paper by Baly and Tuck (Trans., 1908, **93**, 1909).

The spectra of dibenzyl and stilbene exhibit differences analogous to those formerly found between those of cinnamic acid and hydrocinnamic acid (Trans., 1907, **91**, 202). R. V. S.

Absorption Spectra. III. Spectra of Motoisomerides. CECIL R. CRYMBLE, ALFRED W. STEWART, and ROBERT WRIGHT (*Ber.*, 1910, **43**, 1191—1193).—From an examination of the absorption spectra of carefully purified nitrobenzene, in the pure state and in alcoholic solution, made at intervals of a few days, the authors find that no change in the absorption takes place on keeping. The spectrum differs slightly from that given by Baly and Collie (Trans., 1905, **87**, 1332). R. V. S.

Influence of Constitution on the Rotatory Power of Optically Active Substances. III. HANS RUPE (*Annalen*, 1910, **373**, 121—128).—See this vol., i, 398.

Physico-chemical Investigation of Binary Mixtures with an Optically Active Component. OTTO SCHEUER (*Zeitsch. physikal. Chem.*, 1910, **72**, 513—608).—The following nine binary systems,

made up in each case of an optically active and an inactive component have been investigated: Diethyl diacetyltartrate with nitrobenzene, *m*-nitrotoluene, ethylene dibromide, phenol, and naphthalene, and *l*-menthol with nitrobenzene, anethole, methylurethane, and naphthalene. For each of the nine mixtures, the freezing-point curves, the viscosity and expansion curves at different temperatures, and polarimetric measurements with the pure components and their binary mixtures, using light of different wave-lengths, were obtained. The experimental data are given in great detail, being represented in tabular form and also graphically.

The eutectic temperatures for the different mixtures are as follows: Diethyl diacetyltartrate and nitrobenzene, $-1\cdot65^\circ$; the tartrate and nitrotoluene, $+9\cdot85^\circ$; the tartrate and ethylene bromide, $+1\cdot95^\circ$; the tartrate and phenol, $-24\cdot15^\circ$; the tartrate and naphthalene, $43\cdot0^\circ$; menthol and nitrobenzol, $2\cdot60^\circ$; menthol and naphthalene, $31\cdot7^\circ$; menthol and anethole, $13\cdot9^\circ$, and menthol and methylurethane, $32\cdot15^\circ$. In no case is there definite indication of the formation of chemical compounds, although in the first three binary mixtures containing menthol, the existence of very highly dissociated compounds is possible. The complexity of the components is calculated from the freezing-point depressions, on the assumption that the van't Hoff-Raoult law applies. The cryoscopic constants for methylurethane (48·5) and for *m*-nitrotoluene (67·8) were communicated to the author by Beckmann.

The dilatation and viscosity measurements were made by the usual methods, and afford no definite evidence of chemical combination in the liquid state in any of the nine mixtures. It is noteworthy that those mixtures which might contain highly dissociated compounds from the results of the freezing-point measurements show no evidence of chemical combination according to the viscosity and dilatation measurements and conversely.

The majority of the polarimetric measurements were made with the light from a mercury lamp, a ray filter being used to purify the light; some of the results were obtained with the light from an Auer lamp. Results for a number of rays are tabulated. The rotation alters greatly with the concentration and the nature of the solvent. The dispersion coefficients of menthol are practically independent of temperature and concentration, and remain constant for all solvents except nitrobenzene, the deviation in the latter case being probably due to the colour of the nitrobenzene. The dispersion curves of mixtures containing diethyl diacetyltartrate are much more complicated.

As the effect of a solvent in changing the rotation of an optically active substance is not, in the cases under investigation, connected with chemical combination, three other causes may be suggested: (1) that the optically active substances exist in tautomeric forms of different rotatory power; (2) that a deformation of the optically active molecule takes place, connected with alterations in the internal pressure of the solution, and (3) the active molecules may be dissociated or polymerised. Suggestions are made as to how a decision between these alternatives may be reached. G. S.

Photo-electric Sensitiveness of the Alkali Metals as a Function of the Wave-length. II. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1910, **12**, 349—360. Compare this vol., ii, 379)—The anomalous photo-electric behaviour of potassium sodium alloy has led the authors to examine more closely the photo-electric properties of the alkali metals. The metals rubidium, potassium, and sodium in the solid form all show a photo-electric maximum, which corresponds with the wave-lengths $\lambda = 480\mu\mu$, $440\mu\mu$, and $320\mu\mu$ respectively. The maximum at $390\mu\mu$ for a potassium sodium alloy containing 69·4% potassium is so sharp that it cannot be considered as due to a superposition of the maxima observed for the separate elements.

Potassium and sodium amalgams behave quite differently from the free alkali metals. There is no resonance effect in the form of a maximum, and the photo-electric sensitiveness increases regularly with decreasing wave-length of the incident radiation. H. M. D.

Pressure of Light on Gases. PETER LEBEDEFF (*Ann. Physik*, 1910, [iv], **32**, 411—437; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 149—158).—By means of a special form of apparatus the author has measured the pressures which result when light is allowed to fall on various gases. The gases examined were carbon dioxide, methane, ethylene, acetylene, propane, and *n*-butane. On account of the low thermal conductivity of these gases, it was found necessary to mix them with an equal volume of hydrogen, so as to facilitate the equalisation of the temperatures of different portions of the gas. The observed pressures are directly proportional to the energy of the incident light and to the coefficient of absorption of the gas under examination. Within the limits of accuracy of the measurements, the pressures are in agreement with the equation of Fitzgerald: $p = aE/v$, in which p is the pressure due to the light, E the energy of the light incident on the gas in unit time, a the coefficient of absorption of the gas, and v the velocity of light. H. M. D.

The Scattering of α-Particles by Matter. HANS GEIGER (*Proc. Roy. Soc.*, 1910, *A*, **83**, 492—504. Compare Abstr., 1909, ii, 782).—Quantitative measurements have been made on the amount of scattering of the α-particles produced (1) in different thicknesses of the same material; (2) in different materials; (3) with α-particles of different velocity. The results are expressed in terms of the most probable angle of scattering, ϕ, which was determined by counting the number of scintillations at different distances from the centre of a zinc sulphide screen, on which impinge a fine pencil of intense α-rays from radium-*C*, when films of varying thickness and materials were interposed at known distances from the screen. For gold, it was found that, initially, ϕ increased at first more rapidly than the thickness traversed, but after a thickness equivalent to about 1 mm. of air had been traversed, ϕ increased directly as the thickness up to the end of the range. This is explained by the rapid increase of scattering as the velocity of the α-particle diminishes. If each atom of gold

traversed deflected the α-particle by a constant amount, it is deduced that ϕ should increase proportionally to the square-root of the thickness traversed. The most probable angle through which an α-particle is turned by a layer of gold equivalent to 1 cm. of air (called the coefficient of scattering) is 2·1°, or per atom of gold (atomic scattering coefficient) about 0·005°. For tin, silver, copper, and aluminium the relation between ϕ and thickness was similar to that for gold, the scattering coefficients being directly proportional to the atomic weight. The scattering coefficient was found for gold to be inversely proportional to the cube of the velocity of the α-particle, and this rapid increase of scattering, as the end of the range is approached, may play an important part in the apparently sudden stoppage of the α-particles.

F. S.

The Ionisation Produced by an α-Particle. II. Connexion between Ionisation and Absorption. HANS GEIGER (*Proc. Roy. Soc.*, 1910, *A*, **83**, 505—515. Compare Abstr., 1909, ii, 782).—Under improved conditions a re-determination of the diminution of velocity of α-particles in traversing matter has been carried out by measuring the displacement, in a magnetic field, of the fluorescent image produced by a narrow pencil of α-rays of radium-*C* impinging on a zinc sulphide screen. The results agree well with the original ones of Rutherford (Abstr., 1906, ii, 642) up to a range equivalent to 6 cm. of air, but after this indicate a much more rapid diminution of velocity. It is found that the velocity of an α-particle at any point of its path is proportional to the cube-root of the range it has still to run. Up to about 5 mm. from the end of the range, the number of α-particles is undiminished by passage through matter, but after this a rapid regular diminution occurs. That this is not due to initial differences in the velocity at which the α-particles are expelled from the parent atom is shown by a special magnetic deflexion experiment, in which a 0·5 per cent. difference of velocity could have been detected. The differences of velocity at the end of the range are due to the individual chances of collision with gas molecules and to the scattering which takes place. The ranges given by Bragg (7·06 cm. for the α-particle of radium-*C*) are the extreme ranges, and the average range is estimated to be only 6·7 cm. The Bragg curve, of ionisation plotted against thickness of matter traversed, is an average curve for a pencil of α-particles travelling at slightly different speeds, and is not the true curve holding for the individual particle. On the probable and natural assumption, that the ionisation produced by an α-particle is proportional to its loss of energy, the ionisation should vary inversely as the cube-root of the part of the range still to be traversed, and the observed curves for a pencil of α-rays are in good agreement with this view. It follows that the ionisation and the expenditure of energy are inversely proportional to the velocity, or, in other words, to the time taken for the particle to cross the atom, a relation deduced by Bragg from other considerations. In an addendum a slight correction is pointed out, diminishing slightly the number of ions, produced by the α-particles from the different members of the radium series, given in the previous paper.

F. S.

The Ionisation of Various Gases by the β-Rays of Actinium. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1910, *A*, 83, 530—533).—The relative ionisations produced by the β-rays of actinium and uranium respectively in air, hydrogen, ethyl ether, ethyl chloride, ethyl bromide, and ethyl iodide are the same. The β-rays of actinium, being of much lower velocity than those of uranium, it follows that the relative atomic absorptions and ionisation are independent of the velocity of the rays for atoms up to the atomic weight of iodine. F. S.

The Question of the Homogeneity of γ-Rays. FREDERICK SODDY, Mrs. WINIFRED MOLLER SODDY, and ALEXANDER S. RUSSELL (*Phil. Mag.*, 1910, [vi], 19, 725—757. Compare Abstr., 1909, ii, 460, 851).—The absorption curves of the γ-rays of uranium-*X* for seven substances for the first part of the range, up to the equivalent of 1 cm. of lead, have been determined. They are very complex, and vary in character greatly for the different absorbers. They failed to establish the presence of a soft type of primary γ-radiation, and if such exists it must be relatively feeble and unimportant. For radium there is no true evidence of a soft primary γ-radiation. Over the initial ranges of thickness, the form of the absorption curve depends greatly on the experimental disposition employed, and may depart in opposite senses from the simple exponential form according to the nature of the absorber and the conditions. The early experiments which have been interpreted as indicating a soft γ-radiation were done for lead only, but for other substances the absorption curves show that such an explanation cannot be correct.

The source of γ-rays being placed at the centre of a truncated hemisphere of varying thickness and the radiation over the whole solid angle of 180° included, the theoretical absorption curve can be deduced on the assumptions that the rays are homogeneous, that they are exponentially absorbed, and that they are not scattered. The experimental curve found for lead and radium γ-rays agreed almost perfectly with the theoretical, the value of the absorption-coefficient λ being 0·50 (cm.)$^{-1}$. In other cases more or less marked departures from the theoretical curve occurred. For β-rays the absorption law is entirely different, owing to scattering. The variation of the absorption curve from the exponential form observed by Tuomikoski (Abstr., 1909, ii, 533) is due to a very penetrating secondary radiation of peculiar properties. When this is eliminated, the absorption curve is absolutely exponential up to 22 cm. of lead, the value of λ being 0·50. For many substances differences in the experimental disposition and in the previous screening to which the rays have been subjected, whilst not affecting the true exponential character of the absorption, modify greatly the value of λ. The abnormal value of the ratio λ_U/λ_{Ra} for lead, 1·465, before found is so explained. With other arrangements the normal value 1·2 to 1·3 is obtained. The homogeneity of the radium γ-rays, in view of the known heterogeneity of the β-rays, supports the view before expressed that the two types of rays are not interdependent. F. S.

A New Circumstance in the Formation of Cathode-Rays. Louis Dunoyer (*Compt. rend.*, 1910, **150**, 970—973).—In a vacuum tube provided with steel electrodes and a side-tube containing carefully purified sodium, the vacuum was maintained at the highest possible point by a Gaede pump, and the sodium was distilled. After cooling, even at the highest degree of vacuum, the walls showed the cathode-ray fluorescence under the discharge in a great number of small, well-defined, very brilliant patches, which remained perfectly fixed and could be photographed, although the vacuum was far too high for the ordinary cathode-rays to be produced at all. The phenomenon is shown also with platinum, but not with aluminium electrodes. The explanation suggested is that minute drops of distilled sodium on the electrodes, touching them only over a minute area, and therefore thermally isolated, become warm enough under the passage of the discharge to give the Edison effect, the electrons emitted, accelerated by the electric field, constituting well-defined, narrow bundles of intense high-velocity cathode-rays. F. S.

Positive and Negative Ions in Canal-Rays of Hydrogen, Oxygen, and Nitrogen. Wilhelm Wien (*Physikal. Zeitsch.*, 1910, **11**, 377—379).—The fluorescent methods of measuring the magnetic deflexion of the canal-rays can only be carried out in hydrogen and helium, for the fluorescence produced in other gases is too small. Only once in a tube provided with electrodes carefully freed from hydrogen was the magnetic deviability of the oxygen canal-rays observed. A new method described consists in bringing through the path of the beam a Rubens' linear thermopile, by means of a screw actuated from outside. By using two Gaede pumps, the one exhausting the vacuum-tube proper and the other the attached deviation chamber, and allowing a steady stream of the gas to flow into the former, it was arranged that the pressure in the deviation chamber was very low without stopping the discharge. The energy curve for the canal-rays showed at high exhaustion a second maximum, corresponding with the deflected beam. In hydrogen at low pressure, the maximum due to the deflected positive-rays was about 7% of that due to the undeflected beam. The negative ions gave a well-marked maximum only at very low pressure, corresponding with 1% of the undeflected rays. For oxygen, the magnetic field which displaced the energy maximum to the same extent as in hydrogen was four times greater, being proportional to the square root of the atomic weight. Mercury vapour appeared to exert a great influence on the negative ions. F. S.

Radioactive Recoil. Sidney Russ (*Le Radium*, 1910, **7**, 93—96; *Mem. Manchester Phil. Soc.*, 1910, **54**, No. viii, 1—12).—The decay curves of the recoil products collected on a disk suspended 7 cm. above the bottom of an exhausted glass tube, on which radium emanation is kept condensed by liquid air, agree well with the view that the number of atoms of radium-*A* and of radium *B* recoiled is equal, but that of radium-*C* only a relatively very small number of atoms is recoiled.

Since the first two substances both result in α-ray changes, whilst the third results in a change in which no α ray but only slow β-rays are expelled, this is as is to be expected. F. S.

The Range of Radioactive Recoil-Products (Projections). LOUIS WERTENSTEIN (*Compt. rend.*, 1910, **150**, 869—872).—The object was to see whether the particles of radium-*B* recoiled from radium-*A* possessed a definite range like the α-particles. Recoiling atoms of radium-*B* are known to be positively charged, and the plate receiving the recoiled radium-*B* was kept positively charged to repel all particles not arriving with sufficient speed. The results are interpreted in support of the view that the recoiled atoms possess a definite range which is inversely proportional to the pressure, as in the case of the α-particles. The range found was 0·1 mm. of air at normal pressure, which is about 400 times less than the range of the α-particles of radium-*A*. Gold leaves of $0{\cdot}08\mu$ thickness would thus completely stop the recoiling atoms. F. S.

Estimation of Radium by Measurement of the Disengaged Emanation. Mme. MARIE CURIE (*Le Radium*, 1910, **7**, 65—70).—The paper contains a detailed account of methods long in use at the author's laboratory for the estimation of radium by means of the emanation, in quantities of the order of from 10^{-6} to 10^{-9} gram. The methods do not differ in principle from the one most commonly employed.

The best time of accumulation of emanation is found by experience to be between fifteen and forty-eight hours; shorter periods, as is to be expected, are less definite, whilst longer periods unexpectedly also show variations of 5% or more. The preparation of accurate standards of radium is described, the starting point being the pure radium chloride used in 1907 for atomic weight determinations. Great care must be exercised, or the radium is precipitated. After being made a year, even the best standards suffer a gradual loss of radium. Addition of a barium salt is recommended for secondary standards. Some indications of a possible "Radium-*X*" intermediate between radium and its emanation have been obtained. A freshly crystallised radium chloride appears to suffer a slow augmentation in the rate of production of emanation; a solution from which radium has been precipitated by sulphuric acid gave a progressively diminishing rate, although it remained limpid. The calculated saturation current given by the equilibrium accumulation of 1 gram of radium (element) is $3{\cdot}5 \times 10^4$ *E.S.U.* in a cylindrical ionisation chamber, 12·5 cm. high, 6·7 cm. internal diameter, 440 c.c. volume, provided with an axial wire electrode 3 mm. diameter charged to 800 volts. F. S.

Radium, Thorium, and Actinium in the Atmosphere and their Significance in Atmospheric Electricity. KARL KURZ (*Abh. K. Akad. wiss. München*, 1909, **25**, 5—56).—The radioactive matter deposited on a negatively charged wire exposed to the atmosphere can be analysed from the decay curves for varying times of exposure, by means of the disintegration theory, into three components,

due to radium, thorium, and actinium emanations respectively. The proportion depends, not only on the relative quantities of the products respectively present in the atmosphere, but also on the voltage to which the wire is charged, owing to the products possessing different mobilities. The average ratio of the mobility of the thorium and radium products was as 1 is to 2·9. Only the first products of the emanations deposit on the wire, and the later products are formed in situ on the wire, and are not attracted to it from the air. The "Activierungszahl" of Elster and Geitel has been reduced to absolute measure, and the number 1 corresponds with the production of 0·06 ion per c.c. per second by the total radioactive matter in the atmosphere. The suspended radioactive matter in the air accounts for only a small fraction of the ionisation of the atmosphere. F. S.

Physico-chemical Constants of the Mineral Waters "Alturas de Palacios" (Plasencia), Casas de Vés (Alicante), and San Antón (Orihuela). EUGENIO MORALES CHOFRÉ (*Anal. Fis. Quim.*, 1909, 7, 479—482).—The curative waters of "Alturas de Palacios" issue from granite rocks at a temperature of 19·5°, contains only 0·80 gram of mineral matter per litre, and have an initial radioactivity of 1944 volts per hour-litre, and a specific conductivity, 0·00150. The molecular weight of the dissolved solids, calculated from the depression of the freezing point, 0·057°, is 25·96, assuming no dissociation to occur.

The water of the Salaboreja spring at Casas de Vés had a radioactivity, measured more than twelve days after bottling, of 13·7 volts per hour-litre, and contained 3·68 grams of dissolved matter per litre. The specific conductivity was 0·0042643. The water of the Villatoya spring in the same locality had a radioactivity of 15·8 volts per hour-litre. The solid residue is 2·2877 grams per litre, and the specific conductivity, 0·0038288. The water of Corvatilla is not radioactive.

The water of San Antón (Orihuela) has an initial radioactivity of 141·9 v.h.l. W. A. D.

Radioactivity of Medicinal Mineral Waters of the Valencian District. EUGENIO MORALES CHOFRÉ (*Anal. Fis. Quim.*, 1909, 7, 482—484).—The following table shows the results:

Spring and district.	Radioactivity in volts per hour-litre. When measured.	Calculated as initial value.	Time from sampling to making measurements.
Calcium sulphide water:			
Chulilla (V)	20·2	47·1	108 hours
Fuente Podrida (V)	27·5	81·4	140 ,,
Santo Tomás (V)	10·2	96·4	12 days
Santa Ana (V)	34·6	104·2	142 hours
,, ,, (chalybeate)	34·1	102·7	142 ,,
Sodium chloride:			
Nuestra Señora de Orito (A).	35·2	63·5	75 ,,

Spring and district.	Radioactivity in volts per hour-litre. When measured.	Calculated as initial value.	Time from sampling to making measurements.
Sulphurous sodium chloride :			
Molinell (V)	20·3	40·5	88 hours
Sodium hydrogen carbonate :			
Onteniente ; del Rey (V)	97·4	123·9	30 ,,
Calcium hydrogen carbonate :			
Bellús (V)	27·7	38·1	40 ,,
Villavieja (V)	37·6	45·6	24 ,,
Mixed hydrogen carbonates :			
Burjasot (N. S. de la Cabeza) (V)	24·5	31·9	33 ,,
Calcium sulphate :			
Busot, La Cogolla (A)	32·5	51·4	58 ,,
,, San Ignacio (A)	33·6	53·1	58 ,,
Camarena (I)	108·0	108·0	0 ,,
Magnesium sulphate :			
Montanejas (C)	51·8	63 9	26 ,,
Ferrous hydrogen carbonate :			
Siete Aguas (V)	21·9	39 8	76 ,,
Cabiñal (V), artesian well of 30 metres	81·6	81·6	0 ,,
,, artesian well of 100 metres	64·0	64·0	0 ,,
Montanejos (C)	0·0	0 0	34 ,,

(V), (A), (T), and (C) denote the provinces of Valencia, Alicante, Teruel, and Castellón. W. A. D.

The Radioactivity of the Springs of Bad Dürkheim a.d. Haardt. MAX LEVIN (*Physikal. Zeitsch.*, 1910, **11**, 322—324).—Contrary to the observations of Ebler, the emanation derived from the water of Bad Dürkheim has been found to decay exponentially with the period of the radium emanation, although addition of sulphuric acid to the water precipitated no active matter, and did not reduce its emanation-producing power; subsequent addition of barium chloride followed by precipitation with sulphuric acid completely removed the emanation-producing power. This is interesting, as the precipitate first obtained (calcium and strontium, but no barium, is present) weighed ten times as much as the second precipitate, which shows that the presence of barium is necessary for the precipitation of minute quantities of radium. The results, however, disprove Ebler's view that the water contains a new radio-element in the alkali-metal series, giving an emanation of longer period than that of radium. F. S.

Ionisation of the Hot Spring of Hamman-Salahin, near Biskra. ALBERT NODON (*Compt. rend.*, 1910, **150**, 1083—1084).—The spring is situated 6 km. north of Biskra at the foot of the outlying buttresses of Mount Atlas. It gives 1500 litres a minute, and the temperature is 46°. The water contains sodium chloride and sulphide. The unit ionisation in the aluminium electroscope employed was that given by 1 gram of black oxide of uranium. The positive

ionisation given by the water three hours after drawing was 0·1, and the negative ionisation, 0·05 per litre. The polarity of the ionisation of thermal waters appears to be closely connected with their therapeutic and chemical properties. F. S.

The Ionic Mobility in Argon and the Influence of Small Quantities of Oxygen on this Magnitude. J. FRANCK (*Ber. Deut. physikal. Ges.*, 1910, **12**, 291—298).—From the rule that the ionic mobility of a gas is inversely proportional to its molecular weight, argon should have for the positive ion a value 1·22 cm. per sec. for a potential-gradient of 1 volt per cm., and for the negative ion, 1·65. A surface ionisation produced by polonium and a modification of Rutherford's alternating current method previously used for helium (Abstr., 1907, ii, 523) were employed. Whereas the value for the positive ion was found to be 1·37, nearly the calculated value, the value for the negative ion was found to be 206·3 as a maximum, which is more than a hundred times as great as was expected; but it was found that the latter value was extremely sensitive to impurities, derived from the apparatus (built up of sealing-wax, glass, and metal). An addition of a small quantity (1·5%) of oxygen to the argon lowered the mobility of the negative ion to 1·70 (about the calculated value), and further additions up to 10% had no further effect. This result is theoretically very inexplicable. F. S.

Slowness of Recombination of the Ions Produced in Certain Chemical Reactions. HENRI J. PROUMEN (*Bull. Soc. chim. Belg.*, 1910, **24**, 209—210. Compare this vol., ii, 381).—The ions which are formed in processes of combustion with an insufficient supply of oxygen can be detected at the end of two hours after the extinction of the flame. It is probable that the property of discharging an electroscope which is exhibited by the products of combustion is, in part, due to charged solid particles which behave as large ions. The importance of such ions in connexion with atmospheric phenomena is mentioned.

H. M. D.

The Effect of Dust and Smoke on the Ionisation of Air. A. S. EVE (*Phil. Mag.*, 1910, [vi], **19**, 657—673).—The excess of positive over negative ions in the air found by the Ebert apparatus is due to combination of the "small ions," particularly the negative, with particles of smoke, dust, or mist, whereby they are converted into "large ions"; these pass undetected through the apparatus, which measures rather the physical purity of the air than the intensity of ionisation. With a constant ionising source of γ-rays, the value of the ionisation current in the apparatus was found to vary as much as 50% with the purity of the air. The large value found for the ionisation over the ocean, surprising in view of the small quantity of radioactive matter, is probably due to the great purity of the air. A cloud of tobacco smoke or ammonium chloride fumes contains large numbers of charged centres, of feeble mobility, in the absence of radium, and the number of such centres does not appear to be much influenced by intense γ-rays. The transformation of small ions into

large ions through the agency of smoke and flames may increase the total number of ions present while diminishing the conductivity, and the process has an important bearing on the variation of the potential gradient in the atmosphere. F. S.

Ionisation by the Spraying (Pulverisation) of Liquids. LÉON BLOCH (*Compt. rend.*, 1910, **150**, 967—969).—Spraying of the liquids in very fine drops was effected by means of an apparatus of the Gouy type, which has the advantage that the jet does not encounter any solid obstacle, and the Lenard effect of ionisation, due to flattening of the drops of water, is avoided. The spray traversed a very large metallic cylinder, then passed into a flask, where the larger drops deposit, and, lastly, into a cylindrical condenser connected with an electrometer. Only moderate air currents were used, and only the ions of feeble mobility collected. The ionisation currents produced are generally of the same order for the ions of both signs. Distilled water, solutions of dilute hydrochloric acid, concentrated potassium hydroxide, and normal copper sulphate, ethyl and amyl alcohols, and acetone gave an intense ionisation, especially the three last; while other liquids, such as benzene, turpentine, olive oil, and vaselin oil gave no effect. The liquids thus class themselves in the same manner for spraying as for bubbling. F. S.

Ionisation by Bubbling and Chemical Actions. MAURICE DE BROGLIE and L. BRIZARD (*Compt. rend.*, 1910, **150**, 969—970).—The bubbling of a gas through a liquid from a very close fabric, while giving the same ionisation effects as from a narrow tube, reduces the surface agitation, and enables the effect to be studied of superimposing a layer of non-ionising liquid, such as benzene, on a liquid which gives ionisation. By ultra-microscopic and electric observations, it has been established that the bubbles convey an envelope of the lower liquid across the upper liquid. When the bubbles burst, the conveyed liquid falls back to the lower liquid layer. The results bear out the conclusion of Bloch (this vol., ii, 381) that the ionisation of gases by chemical action is essentially the same as the ionisation by bubbling. It is found that a certain number of centres carry multiple charges, which endow them with considerable mobility in spite of their large size. F. S.

Ionisation in Gases through Mechanical Division of Liquids: Active and Inactive Substances. MAURICE DE BROGLIE (*Compt. rend.*, 1910, **150**, 1115—1118. Compare Abstr., 1907, ii, 664; 1909, ii, 207, 537, 637; this vol., ii, 11; Bloch, this vol., ii, 381).—A discussion of results already published, with an account of fresh experiments showing that whatever method is adopted for mechanically separating liquids into small particles (shaking, splashing, spraying from a jet, etc.), the ionisation so produced in the gas in which the operation is effected is always of the same character, and in each case the liquids employed may be divided sharply into two classes, active and inactive. Activity appears to be connected with the presence of water in the substance showing this property. W. O. W.

Specific Velocity and Recombination of the Ions in Hexane. GEORGE JAFFÉ (*Ann. Physik*, 1910, [iv], 32, 148—178. Compare Abstr., 1909, ii, 208).—With the object of ascertaining to what extent the phenomena of electrical conduction in dielectric liquids are analogous to those exhibited by gaseous conduction, the author has investigated the conductivity of hexane when subjected to the influence of radium rays. By a method similar to that employed by Langevin, it is found that the specific velocities of the positive and negative ions are respectively $6{\cdot}03 \times 10^{-4}$ and $4{\cdot}17 \times 10^{-4}$ cm. per second. The coefficients of diffusion calculated from these numbers are $1{\cdot}50 \times 10^{-5}$ and $1{\cdot}03 \times 10^{-5}$. The data obtained in the examination of the rate of recombination of the ions cannot be satisfactorily represented by the equation of Thomson or by that of Sutherland. On the other hand, these results are in agreement with the empirical equation : $dn/dt = -a.n^{1{\cdot}84}$, in which $a = 1{\cdot}36\epsilon^{0{\cdot}84}$, and ϵ is the charge on the ions. H. M. D.

Conduction of Electricity in Solid Elements and Compounds. I. Resistance Minima, Electronic Conduction, and the Application of Dissociation Formulæ. JOHANN KOENIGSBERGER and K. SCHILLING (*Ann. Physik*, 1910, [iv], 32, 179—230).—The nature of the process of electrical conduction in silicon, titanium, and zirconium, in metallic oxides and sulphides, and in aromatic organic compounds has been investigated. By measurements of the conductivity at different temperatures, it has been found that a maximum conductivity is reached at a particular temperature both in the case of elements and compounds. This maximum has no connexion with a transition temperature, and is attributed to electronic dissociation.

From the conductivity data in combination with polarisation measurements, the authors conclude that the electrical transport in the solid elements, oxides, and sulphides, and in certain liquid aromatic compounds examined, is entirely due to electrons. In the case of solid compounds of pronounced saline, acidic, or basic character, the conduction is in part attributable to ions. H. M. D.

Conduction of Electricity through Glass. MAX LE BLANC and FRITZ KERSCHBAUM (*Zeitsch. physikal. Chem.*, 1910, 72, 468—507). —Warburg's experiments (compare Abstr., 1884, 1241) on the conduction of electricity through glass have been repeated and extended. In the investigation, plates of sodium glass, 0·1—1·0 mm. in thickness, were used, and the electrodes were of mercury. The method of measurement is fully described.

When sodium glass, 1·0 mm. thick, is electrolysed at temperatures in the neighbourhood of 300°, the current rapidly diminishes, owing to the formation of a white, badly conducting layer (in one experiment 0·03—0·045 mm. thick) near the anode. A plate 0·1 mm. thick was completely converted into this badly conducting material by prolonged electrolysis. In preparing this material, only the sodium ions are discharged, and in the proportion calculated from the current, the silicate ions give up their charges without decomposition.

The conduction of electricity through the badly conducting material is not accompanied by the transport of matter, and Ohm's law does not

hold, the current being proportional to the square of the applied *E.M.F.* On electrolysing the new material in contact with 1% sodium amalgam, the original glass is reformed by the introduction of sodium ions. For reasons not fully understood, the regeneration of the glass is effected much more readily than its decomposition.

At the temperature of the experiment, no gas is given off at the anode, but on heating the resulting material to the temperature of softening, an amount of oxygen is obtained nearly equivalent to the amount of sodium liberated during the electrolysis. The migration velocity of the sodium ions in glass at 320° is about 1×10^{-8} cm./sec. for a difference of potential of 1 volt per cm. G. S.

Electron Theory and Solid Solutions of Metals. RUDOLF SCHENCK (*Ann. Physik*, 1910, [iv], **32**, 261—290).—A theoretical paper in which an explanation is given of the diminution of the electrical conductivity and of the increase of the ratio of the thermal to the electrical conductivity in the case of metallic solid solutions. According to this, the diminished electrical conductivity is not due to a decrease in the number of the electrons, but to an increase in the viscosity of the medium. Thermo-electric effects obtained by pairing the pure metals with their solid solutions are cited in favour of the author's theory. H. M. D.

Electrical Conductivity of Certain Hydroxamic Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1910, **40**, i, 102—107).—According to Palazzo and Tamburello (Abstr., 1907, i, 298), formhydroxamic acid must be regarded as having the structure $\begin{matrix} OH\cdot N \\ | \\ CH_2 \end{matrix}\!\!>\!O$. From measurements of the electrical conductivity of a number of homologous hydroxamic acids, the author draws the conclusion that all of these acids have a structure similar to that of the first member of the group. The following values have been obtained for K: formhydroxamic, 0·000010; acethydroxamic, 0·0000028; propionhydroxamic, 0·0000028; butyrhydroxamic, 0·0000023; oxalhydroxamic, 0·000019; malonhydroxamic, 0·0000066; benzhydroxamic, 0·000075; anishydroxamic, 0·000073; salicylhydroxamic, 0·00064. These acids are hence only very slightly dissociated in solution; thus, for $V = 58$, acethydroxamic acid is dissociated to the extent of 0·3%, whilst for acetic acid the amount is about 3%. Also, the molecular weight of formhydroxamic acid can be determined in aqueous solution, the value 57 having been obtained instead of the theoretical number 61. Leaving aside the dibasic hydroxamic acid and also benz- and salicyl-hydroxamic acids, in which the acid character is increased by the electro-negative phenyl radicle and by the phenolic hydroxyl group, the constants for the homologous hydroxamic acids are of about the same order of magnitude as those of the weaker acids, and are intermediate to hydrogen sulphide and boric acid. The constants for form-, acet-, and butyr-hydroxamic acids do not differ more than the corresponding values for formic, acetic, and butyric acids, and the author therefore assumes that these hydroxamic acids have similar structures.

T. H. P.

Transport Phenomena in Solutions of Colouring Matters. LÉO VIGNON (*Compt. rend.*, 1910, **150**, 923—925; *Bull. Soc. chim.*, 1910, [iv], **7**, 383—385. Compare this vol., ii, 273).—Experiments on the electrolysis of solutions of dyes have shown that transport phenomena are well marked with those substances which form colloidal solutions, but are absent in the case of dyes forming true solutions.

W. O. W.

Measurement of Magnetic Susceptibility of Solids. PAUL PASCAL (*Compt. rend.*, 1910, **150**, 1054—1056. Compare this vol., ii, 179).—The magnetic susceptibility of a liquid may be measured by placing it in a thin-walled test-tube suspended from one arm of a balance between the poles of a powerful electromagnet. When the field is established, the equilibrium of the beam is disturbed, and weights must be added to the balance pan to bring the surface of the liquid back to its initial position as seen with a microscope. The force amounts to 0·0015 to 0·0060 gram with ordinary organic liquids in a field of 10,000 to 20,000 gauss, but attains to several hundred grams with certain ferruginous solids. The susceptibility can be calculated directly from the dimensions of the tube or indirectly by comparison with water under the same conditions with an accuracy of one part in 150.

R. J. C.

Thermo-magnetic Properties of Elements. H. E. J. G. DU BOIS and KÔTARÔ HONDA (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **12**, 596—602).—Measurements have been made of the variation with temperature of the magnetic susceptibility of about fifty elements. The elements are grouped according as the susceptibility increases, decreases, or remains constant as the temperature rises. The results indicate that the conclusions drawn by Curie in a previous investigation are devoid of any general validity. When liquefaction takes place, a discontinuity in the susceptibility-temperature curve is sometimes observed. This may consist in an alteration of the magnitude of the susceptibility, as in the case of phosphorus, silver, tin, antimony, tellurium, gold, thallium, lead, and bismuth, or in a sudden change in the value of the temperature-coefficient, as in the case of magnesium, copper, cadmium, and iodine.

Polymorphic changes are also frequently accompanied by changes in the magnetic susceptibility, as in the case of tin at 18° and thallium at 234°. On the other hand, the transformation of tetragonal into rhombic tin at 161° is not accompanied by any noticeable change in the susceptibility.

H. M. D.

Simple Apparatus for Determining Melting Points. THEODOR WEYL (*Chem. Zeit.*, 1910, **34**, 488).—A thermometer is slightly expanded just above the bulb. A glass ring loosely fitting the thermometer stem rests on the expansion; it carries glass hooks placed vertically in pairs, these serving to hold the melting-point tubes in position close to the bulb. By this means the attachment of the melting-point tubes to the thermometer stem by platinum wire or india-rubber rings is avoided.

L. DE K.

Freezing-point Measurements on Small Quantities of Liquids. RICHARD BURIAN and KARL DRUCKER (*Zentr. Physiol.*, 1910, **23**, 772—777).—Kinoshita's method (Abstr., 1908, ii, 810) for the determination of the freezing point of small quantities of liquids has many sources of error, perhaps the most important being the total lack of stirring during the determination. The method devised by Guye and Bogdan (Abstr., 1904, ii, 391) is much more trustworthy, but the accuracy with which the thermometer can be read is insufficient for many purposes. The authors use a thermometer the mercury bulb of which is 9 mm. long and 7 mm. in diameter, which gives a scale length of 2·7 cm. per degree; it is divided into fiftieths of a degree, and possesses a range of $-5°$ to $+1°$; the accuracy of reading is 0·002° to 0·005°. The apparatus used is similar to that of Beckmann and Guye and Bogdan, but only 1·5 c.c. of liquid are necessary for a determination. For accurate results strict attention must be paid to the temperature of the freezing-bath, which must never be more than 2° below the freezing point of the liquid under investigation.

The results agree with those obtained with the Beckmann apparatus to within $\pm 0·005°$. T. S. P.

Sublimation by the Dynamical Method. F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1910, **72**, 451—467).—It has already been suggested (compare Smits and Scheffer, Abstr., 1909, ii, 21) that the further investigation of the instances given by Ramsay and Young (*Phil. Trans.*, 1886, **177**, 71), in which the vapour pressures of substances as determined by dynamic and static methods do not coincide, may throw some light on the well-known results of Baker and of Abegg and Johnston on the vapour pressures of dry and moist ammonium chloride. In this connexion, an attempt has been made to determine the sublimation curve of ammonium carbamate, but it was found that there is no true dynamic curve, the results being very irregular and depending on a variety of circumstances. This may possibly be explained on the assumption that the sublimation process is a combination of two velocities, that of evaporation and that of dissociation in the vapour phase.

Ramsay and Young state that aldehyde–ammonia gives regular and distinct pressure-temperature curves by the dynamic and static methods, but this view can no longer be upheld, as the author finds that the dissociation of aldehyde–ammonia is not reversible.

The modifications which must be made in Roozeboom's space figure as a consequence of the recent observations on the vapour density of dry and moist ammonium chloride are discussed. G. S.

Rechenberg's Views as to the Vaporisation occurring in the Cathode Light Vacuum as a Proof of the New Theory of Volatilisation. FRIEDRICH KRAFFT (*J. pr. Chem.*, 1910, [ii], **81**, 425—440).—Mainly polemical in reply to Rechenberg (Abstr., 1909, ii, 544; this vol., ii, 101). C. S.

Boiling in a Vacuum Regarded as the Formation of an Atmosphere. FRIEDRICH KRAFFT (*J. pr. Chem.*, 1910, [ii], **81**, 440—451. Compare preceding abstract).—A further reply to Rechenberg (*loc. cit.*), and a claim for priority over Siepermann (this vol., ii, 267). C. S.

Apparatus to Facilitate Distillation with a Fractionating Column under Reduced Pressure and with a Fixed Flame. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1910, [iv], **7**, 273—277).—In using the ordinary fractionating column for distillation under reduced pressure, a fairly long layer of liquid often forms in the column, causing a considerable difference in pressure between the atmosphere in the distillation vessel and that in the receiver. To avoid this, the author has devised a special form of apparatus, in which the column is too wide to permit of the formation of a long layer of condensed liquid, and provided with a side-tube, which places the distilling vessel and the receiver in independent communication, and thus secures a common atmosphere to both. To prevent "priming," a Bunsen burner provided with a cap, carrying lateral apertures to form horizontal flames, is used. T. A. H.

Shaking Machine for Boiling with a Reflux Condenser. P. J. MONTAGNE (*Chem. Weekblad*, 1910, **7**, 375—377).—This machine is constructed like a child's swing, the condenser, flask, retort ring with wire gauze, and burner being clamped to the movable swing supports, which are joined at the bottom by a cross piece, and connected with an arm which serves to transmit the power in the ordinary manner. A. J. W.

Relationship between Constitution and Heats of Combustion of Unsaturated Hydrocarbons. KARL AUWERS and WALTER A. ROTH (*Ber.*, 1910, **43**, 1063—1064).—As the result of experiments, details of which will be published later, the following generalisations are drawn: (1) Hydrocarbons with conjugate double linkings always have smaller heats of combustion than isomerides in which the olefine linkings are not in conjugate positions. Such compounds therefore possess less chemical energy or are more saturated than their isomerides (compare Thiele). In the case of terpenes, the difference between the heats of combustions of isomerides is usually 2—3%, but in the case of styrenes and the isomeric propylene compounds the amount is only 0·6—0·7%. (2) The presence of substituents attached to the carbon atoms of a conjugate system always increases the heat of combustion of the hydrocarbon, namely, diminishes its degree of saturation. The amounts, however, are comparatively small.
J. J. S.

Heat of Combustion and Relative Density of Methylamines. JOSEPH A. MULLER (*Ann. Chim. Phys.*, 1910, [viii], **20**, 116—130. Compare Abstr., 1885, 716; 1886, 409; Lemoult, Abstr., 1907, ii, 10).—The original contains full experimental details and data in connexion with the determination of the densities and heats of

combustion of methylamine and di- and tri-methylamine. The observations were carried out with more elaborate precautions than in the author's earlier experiments, in order to avoid the possible formation of carbon monoxide. W. O. W.

Determination of Heat Liberated on Addition of Bromine to Unsaturated Compounds. WLADIMIR F. LUGININ (*Compt. rend.*, 1910, **150**, 915—918).—The amount of heat developed by the addition of one molecule of bromine to one molecule of certain unsaturated compounds has been measured, the reacting substances being dissolved in carbon tetrachloride. The following results are recorded: *sec.*-octylene, 28,406 cal.; styrene, 24,003 cal.; *cyclo*hexene, 29,007 cal.; 1-methyl-Δ^3-*cyclo*hexene, 29,188 cal.; ethyl phenylpropiolate, 29,120 cal.; pulegone, 21,897 cal. Except in the case of styrene, which forms a solid dibromide, the corrections necessary to obtain the thermal equivalents are negligible. The heat of dissolution of styrene dibromide is $-5,145$ cal.

Attention is drawn to the influence of the cyclic grouping in raising the value for the thermal equivalent, and to the depressing influence of the ketone group on this constant. W. O. W.

Internal Friction of Metals at Low Temperatures. CHARLES E. GUYE and H. SCHAPPER (*Compt. rend.*, 1910, **150**, 962—964. Compare Guye and Freedericksz, this vol., ii, 21).—The internal friction of copper, zinc, gold, nickel, palladium, and platinum has been measured at 100°, 50°, 0°, $-80°$, and $-195°$ by the torsion pendulum method previously described. As the temperature falls, the viscosities of zinc and copper decrease like that of silver. Gold, as previously noted, exhibits a striking increase in viscosity between $-80°$ and $-195°$. The values with nickel, palladium, and platinum are so small that no certain conclusion could be drawn, but a series of experiments with nine different platinum wires pointed to a higher viscosity at 0° and $-80°$ than at 100° and $-195°$. The modulus of elasticity in all cases increases steadily as temperature falls, but the internal friction, which varies as the distortion, may be greatly affected by loading, previous annealing, etc. R. J. C.

Constitution of Certain Iodine Compounds. Phenomena of Adsorption. HANS SIEGRIST (*J. Suisse Chim. Pharm.*, 1910, **48**, Reprint 9 pp.).—From a consideration of experimental data relating to the removal of iodine from its aqueous solutions by starch, basic lanthanum acetate, tannin, methylene-blue, safranine, dimethylaminophenyldimethylpyrazolone hydriodide, and benzidine dihydriodide, the author arrives at the conclusion that the processes are controlled in a large measure by the phenomenon of adsorption.

If x milligram-equivalents of iodine are adsorbed by a grams of one of the above substances from a solution containing c milligram-equivalents per c.c., then $x/a = \beta . c^m$ in which β and m are constants. The following values of β and m are deduced from the experimental data: basic lanthanum acetate, $\beta = 31.5, m = 0.978$; tannin, $\beta = 6.0, m = 0.15$; methylene-blue, $\beta = 26$, $m = 0.084$; safranine, $\beta = 17$, $m = 0.1$; di-

methylaminophenyldimethylpyrazolone hydriodide, $\beta = 66$, $m = 0{\cdot}2$; benzidine dihydriodide, $\beta = 71, m = 0{\cdot}16$.

For small values of m the adsorption process corresponds closely with the relationships which would be expected if a definite compound were formed. On the other hand, if m is nearly equal to unity, the adsorption phenomena differ only slightly from what would be found if a solid solution were formed.

Küster's data for the removal of iodine from solution by starch indicate that the process is one of adsorption, the values of the constants being $\beta = 3$ and $m = 0{\cdot}1$. H. M. D.

Osmotic Experiments with Collodion Membranes. J. HOWARD MATHEWS (*J. Physical Chem.*, 1910, **14**, 281—291).—Membranes were prepared by pouring a layer of collodion solution on mercury. The half-dried films were stretched over a thistle funnel, and the joint was painted with fresh collodion solution. Such membranes when thoroughly dried from ether and alcohol were tight and strong, and gave no evidence of mechanical leaks. The thickness varied from 0·002 to 0·004 in. Carbon tetrachloride, chloroform, carbon disulphide, and hydrocarbons do not affect these membranes, and do not pass through them. The alcohols exert a solvent action which decreases from methyl to *iso*amyl alcohol. Measurements could be made with 96% ethyl alcohol, but absolute alcohol is very destructive to the membrane. Not only are the alcohols capable of diffusing through collodion, but they assist other substances to pass through. A membrane saturated with 96% ethyl alcohol is capable of passing iodine, copper oleate, and mercuric chloride, which are soluble in alcohol. Water soaks into collodion to a slight extent after long immersion, and the wet membrane is able to pass sugar, glycerol, iodine, and boric and oxalic acids.

A solution of copper oleate in *iso*amyl alcohol was placed within the osmometer and carbon disulphide without. Alcohol passed out, but carbon disulphide attracted by the oleate and assisted by the alcohol passed in so much more rapidly that the level inside rose more than eighty inches. *iso*Amyl alcohol is itself assisted through collodion by *o*-cresol.

In many experiments the solute diffused out through the membrane almost as quickly as the solvent diffused in, hence the observed osmotic pressures were small. The author draws the conclusion that the direction and extent of osmotic action is largely a question of relative solubility. The process is akin to distribution. Osmotic action consists of a major and minor current in opposite directions, as was pointed out by Kahlenberg (Abstr., 1906, ii, 337). Stirring the liquids bathing the membranes serves to hasten the osmotic process.

R. J. C.

Colour and Hydration. I. G. POMA (*Gazzetta*, 1910, **40**, i, 176—193).—The author discusses the work of Magnanini, Hantzsch, Abegg, Jones, and others on the colour of salt solutions and hydration of the salt molecules. According to Hantzsch, a chemically saturated, coloured electrolyte undergoing no change in constitution on dilution

should exhibit normal optical behaviour as indicated by Beer's law, no matter what its degree of dissociation; in other words, the power of absorbing light possessed by the coloured ion is equal to that of the non-dissociated molecule. The author has investigated, by means of a polarisation spectrophotometer, certain coloured salts under conditions not previously employed.

Nickel sulphate solutions of various concentrations varying from 0·149 to 2·384*N* were examined for the parts of the spectrum corresponding with $\lambda = 460$, 602, and $622\mu\mu$, constant values for the molecular extinction being obtained in each case. A similar result is obtained for a 0·9215*N*-solution of nickel sulphate in 0—2·54*N*-sulphuric acid (compare Hantzsch, Abstr., 1908, ii, 14, 462; 1909, ii, 18, 973). As the degree of dissociation of nickel sulphate in these different solutions must vary considerably, Hantzsch's views are confirmed. Somewhat less regular is the optical behaviour of nickel chloride.

Also, solutions of nickel sulphate of different concentrations in about 10*N*-ammonia solution show constant molecular extinctions, so that there exists in the solutions only one metal-ammonia compound,

$$Ni(NH_3)_4SO_4.$$

Similar results are yielded by other nickel salts. When the concentration of the ammonia is gradually increased, the extinction in the green ($556\mu\mu$) remains unchanged, but in the red ($622\mu\mu$) and yellow ($589\mu\mu$) it decreases at first, and becomes constant when the concentration of ammonia reaches about 9*N*.

When the amount of sulphuric acid present in a nickel sulphate solution is increased considerably, the absorption increases rapidly in the blue and violet regions of the spectrum, and shows progressive diminution in the yellow and red; the colour of the solution changes, at the same time, from emerald-green towards chrome-yellow, and, after some hours, part of the salt is deposited as an anhydrous, yellow powder. Similar results are given by solutions of nickel chloride containing increasing proportions of hydrochloric acid. Copper sulphate, in solutions containing larger and larger amounts of sulphuric acid, at first maintains its absorptive power unaltered, but ultimately the colour fades away entirely. The change in colour of cobalt sulphate solution by sulphuric acid is less marked than with the above salts.

The fact that the colours of these anhydrous salts are the same as those of their sulphuric acid solutions indicates that the colours of the anhydrous ions are those of the anhydrous, non-dissociated molecules, whether these are or are not in solution; the ion $Ni^{\cdot\cdot}$ is hence yellow, $Cu^{\cdot\cdot}$ colourless, and $Co^{\cdot\cdot}$ reddish. The characteristic colours exhibited by these ions in aqueous solution are due to their hydrates: $Ni(H_2O)_n^{\cdot\cdot}$, $Cu(H_2O)_m^{\cdot\cdot}$, and $Co(H_2O)_p^{\cdot\cdot}$. T. H. P.

Formation, Equilibrium, and Alterations of Crystals in an Isothermal Medium. P. N. PAWLOFF (*Zeitsch. physikal. Chem.*, 1910, **72**, 385—410).—A mathematical paper dealing with crystal formation from the point of view of Willard Gibbs, but the energy of the angles is taken into account as well as that of the surfaces.

The thermodynamical conditions for the appearance of crystals are developed, and the decision as to which new system will form from a given liquid is made by means of Ostwald's rule that the successive stages make their appearance in the order of the smallest diminution of free energy. G. S.

The Re-formation of the Crystalline from the Amorphous Condition on Heating Pyrognomic Crystals. TH. LIEBISCH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 350—364).—The heating curves of different pyrognomic minerals have been investigated, the thermal effects being followed by means of a platinum–platinum rhodium thermocouple. The minerals used were gadolinite from Ytterby, samarskite, æschynite, and pyrochlore from Miask, euxenite from Arendal, tritomite from the syenite of Langesundfjord, and orthite from Ytterby. All of them, with the exception of orthite, show the pyrognomic phenomenon, and at the point where they begin to glow there is a rapid rise in temperature, due to the development of heat. This development of heat is connected with the change from the amorphous to the crystalline condition, and is independent of whether helium is liberated or not. The thermo-luminescence of fluorspar is unaccompanied by a development of heat; this is not surprising, since there is no change from the amorphous to the crystalline condition. T. S. P.

The System Water–Ammonium Nitrate–Silver Nitrate. FRANS A. H. SCHREINEMAKERS and (Miss) W. C. DE BAAT (*Chem. Weekblad*, 1910, 7, 259—264).—An application of Schreinemaker's graphic method to the system water–ammonium nitrate–silver nitrate at ordinary pressure and between $-19°$ and $110°$. Above $125°$ ammonium nitrate is regular, below this temperature rhombohedral. Another form is rhombic, and exists in two modifications, α and β. At $85{\cdot}4°$ the rhombohedral changes to the α-rhombic form, and this passes into the β-rhombic modification at $32°$. The *double* salt, $NH_4NO_3,AgNO_3$, has been isolated, and a detailed investigation of the composition of the solutions produced at various temperatures between the limits named has been made. A. J. W.

The Transformation Point of Double Salts. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1910, 7, 197—203. Compare Foote and Bristol, Abstr., 1904, ii, 658).—The author has applied his graphic method to the system water–mercuric chloride–barium chloride. In a system containing the hydrated salts A_1 and B_1, which form the double salt D, and water there are three possibilities; D may be formed from A_1 and B_1 either with elimination or addition of water, or without elimination or addition of water. A solution in which the system A_1+B_1+D is in equilibrium is called by the author *congruent* when it consists of these components only, *dilute* when it contains more water than that corresponding with A_1+B_1+D, and *concentrated* when it contains less water. At constant pressure the equilibrium

$A_1 + B_1 + D +$ solution is non-variant. For dilute solutions three reactions are possible:

1. $A_1 + B_1 \rightleftharpoons D +$ solution;
2. $D \rightleftharpoons A_1 + B_1 +$ solution;
3. $A_1 + D \rightleftharpoons B_1 +$ solution.

For congruent solutions the reaction is:

4. $A_1 + B_1 + D \rightleftharpoons$ solution.

When no new phase is formed, as in (4), the author calls the solution *monogenetic*; when one new phase is formed, as in (1) and (3), *bigenetic*; and when two new phases are formed, as in (2), *trigenetic*.

In the system water–mercuric chloride–barium chloride a *double* salt, $BaCl_2,3HgCl_2,6H_2O$, is formed from $BaCl_2,2H_2O$ and $HgCl_2$, which is in equilibrium with its components at 17·2° (Foote and Bristol, *loc. cit.*). The solution is trigenetic. At 0° the solution (24·05% $BaCl_2$ + 46·1% $HgCl_2$) is saturated with $BaCl_2,2H_2O$ + $BaCl_2,3HgCl_2,6H_2O$. At 30° the solution (23·2% $BaCl_2$ + 55·2% $HgCl_2$) is in equilibrium with $BaCl_2,2H_2O + HgCl_2$, and at 40° (22·98% $BaCl_2$ + 56·57% $HgCl_2$) with $BaCl_2,2H_2O + HgCl_2$.

A. J. W.

Velocity of Reaction between Copper Sulphate and Potassium Iodide. E. Oliveri-Mandalà (*Gazzetta*, 1910, **40**, i, 107—112).—In dilute solutions, copper sulphate and potassium iodide react with liberation of iodine at a measurable velocity, which diminishes as the dilution increases: $2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$. According to Traube (Abstr., 1884, 962) this reaction results first in the formation of cupric iodide, which remains unchanged in very dilute solutions, but in more concentrated ones is decomposed into cuprous iodide and iodine with a velocity increasing with the concentration. According to the author's measurements, the reaction between copper sulphate and potassium iodide is of the third order, although six molecules take part in it. By applying van't Hoff's formula for cases in which disturbing actions prevent the order of a reaction from being ascertained, namely,

$$n = \{\log(dC/dt) - \log(dC'/dt')\}/(\log C - \log C'),$$

where $C = A - x$ is the variable concentration at time t, and n the order of the reaction, the latter is found to be 3, the actual values obtained varying from 2·9 to 3·6. The velocity of formation of iodine is approximately proportional to the concentration of the copper sulphate and to the square of the concentration of the potassium iodide; hence the reaction is expressed by the equations: $CuSO_4 + 2KI = CuI + K_2SO_4 + I$ and $I + I = I_2$, or, assuming the preliminary formation of cuprous iodide, by $CuSO_4 + 2KI = CuI_2 + K_2SO_4, CuI_2 = CuI + I$, and $I + I = I_2$. The electrolytic dissociation theory is incapable of indicating which of these two schemes is the correct one, since the equations $Cu + 2I = CuI + I$ and $Cu + I + I = CuI + I$ are identical.

T. H. P.

Atomic Weight Accurately a Function of the Volution of Ideal Space-symmetry Ratios. Newman Howard (*Chem. News*, 1910, **101**, 181—182, 205).—The author shows that the numbers

representing the accepted atomic weights of a considerable number of elements can be accurately represented as functions of numbers which represent the distance ratios characteristic of the crystalline forms of the regular system.

In the second paper, further equations connecting atomic weights and the so-called space-symmetry ratios are given. The author supposes that the different values obtained for the ratio of the combining weights of hydrogen and oxygen are not errors of experiment, but depend on the variation of the space-ratios according to the particular method of synthesis used in the determination. H. M. D.

Genetic Connexions between the Chemical Elements. JAMES MOIR (*S. African J. Sci.*, 1910, 188—191. Compare Trans., 1909, 1752; Abstr., 1909, ii, 562; Loring, Abstr., 1909, ii, 392, 562).—The author's previous work on the subject is summarised, and a number of new relationships between the atomic weights are pointed out.

Besides numbers of the form $4n$ and $4n-1$, nearly all numbers of the form $7n$ also occur, where n is a whole number, and in this way all the atomic weights except 13 are accounted for.

Many examples of exact relations between atomic weights are quoted. These are, however, best shown by the existence of series of elements with a constant difference from a lower series. Thus, besides the well-known differences of 47 and 88, differences of 23·8, 18·8, 68, and others are pointed out. In some cases there is a connexion between the magnitude of the difference and the valency; thus, in the members of the 68 series, $Ag = Ca + 68$, $Cd = Sc + 68·3$, $In = Ti + 67\frac{1}{2}$, etc., the valency of the 68 complex is -1.

A number of illustrations are also given of the fact that the sum of the atomic weights of a number of pairs of elements is equal. G. S.

Relation between the Atomic Weights of Different Groups of the Periodic System. K. SCHERINGA (*Chem. Weekblad*, 1910, 7, 407—409).—In the halogen group are found the following relations:

$$F = 19 = 14 + (2 \times 2\tfrac{1}{2}).$$
$$Cl = 35·5 = (2 \times 14) + (3 \times 2\tfrac{1}{2}).$$
$$Br = 80 = (5 \times 14) + (4 \times 2\tfrac{1}{2}).$$
$$I = 127 = (8 \times 14) + (6 \times 2\tfrac{1}{2}).$$

For cyanogen:

$$(CN)_2 = 52 = (3 \times 14) + (4 \times 2\tfrac{1}{2}).$$

Manganese cannot be brought into the scheme. Analogous relationships are shown for the other groups of the periodic system, for example:

$$O = 16.$$
$$S = 2 \times 16.$$
$$Se = 5 \times 16\ (-1).$$
$$Te = 8 \times 16.$$

A. J. W.

Energy of the Elements and the Part Remaining in Combinations. Energy Theory of Isomerism. ANTONIO QUARTAROLI (*Gazzetta*, 1910, **40**, i, 325—379. Compare Abstr., 1904, ii, 538).—When two elements, A and B, combine, the quantity of energy lost by A depends on B, and that lost by B depends on A, the total energy developed being a function of A and B, $\phi(A,B)$. In the formation of

a compound, ABC, from (1) AB and C, and (2) BC and A, the amounts of energy evolved will, in general, be different in the two cases, that is, $\phi(AB)+\phi(AB,C)$ will not be equal to $\phi(BC)+\phi(BC,A)$; the energy-contents of the two compounds, ABC, will, therefore, be unequal, and the compounds will be isomeric in the sense of Ostwald's conception of isomerism. The author represents the different elements by so many vectors, the length of each of these representing the total energy contained in the atom of the element and the direction the particular tendency which the element has of yielding more or less energy in combining with one rather than with another element. On this foundation, a system is developed of determining energy constants which represent the transformations of energy occurring in chemical processes, just as the atomic constants represent the weight relations. For a number of elements values are given representing the energy constant, $r=\sqrt{x^2+y^2+z^2}$, and the three vector-components, x, y, and z, and it is shown how an approximate representation may be obtained of the differences between the heats of formation of fluorides and chlorides, chlorides and iodides, chlorides and bromides, chlorides and oxides, chlorides and hydrides, etc. The method is applied also to the residual energy of combined elements and combination of compounds with elements or compounds, such as the union of oxides and anhydrides with oxygen, to water of crystallisation, double salts, molecular combination of neutral salts with acids, etc.

The experimental investigations show that the slightly soluble salts of dibasic or, in general, polybasic acids occur frequently in two forms: (1) a voluminous, amorphous form, in which the metallic atoms are united unequally to the acid residue, so that one may be separated before the other with formation of an acid salt, and (2) a crystalline form, in which the metallic atoms are united similarly to the acid residue, and can only be displaced simultaneously, a deficiency of a strong acid liberating only free acid. Thus there exist two forms of dicalcium (or dibarium) phosphate, one transformable by gradual addition of hydrochloric or phosphoric acid into the monocalcium phosphate, and the other not so transformable; the former is capable of combining with a further quantity of lime to give tricalcium phosphate, the latter not. Also, trilithium phosphate exists in two forms; one, the more soluble, hydrolysable and transformable into the dilithium salt, and the other, non-hydrolysable and giving only monolithium phosphate, even with deficiency of acid.

It is shown that, in general, with inorganic compounds, although the theory of valency can, in certain cases, establish numerical relationships between the atoms entering into combination, yet it is not adapted to furnish structural formulæ in accord with the reactions and energy relations of the compounds. This is the case even with the more simple compounds, and especially so as regards the formulæ of complex minerals. T. H. P.

The Nature of the Forces of Attraction between Atoms and Molecules. R. D. KLEEMAN (*Phil. Mag.*, 1910, [vi], 19, 783—809).—Starting from the assumption that the attraction between two molecules of the same kind is given by $\phi(z)(\Sigma c_a)^2$, where $\phi(z)$ is a

function of the distance between the molecules, and Σc_a is the sum of a number of constants each of which refers to an atom of a molecule and is independent of all conditions except the nature of the atom, a number of expressions have been developed on the same lines as has been done by Einstein, and the values of c_a for the different atoms involved have been found from one of these expressions for numerous compounds from the data of Ramsay and Shields. This value is proportional to the square root of the atomic weight or to the chemical valency (Traube). With regard to the function $\phi(z)$, it is deduced that for distances below a centimetre the attraction probably varies inversely as the fifth power of the distance of separation of the molecules. The conditions for two molecules separating after collision instead of remaining combined is that the kinetic energy of either must be greater than the potential energy due to their attraction when they are in contact. This gives for the inferior limit of the distance of separation of two hydrogen molecules at 0°, a value $1 \cdot 34 \times 10^{-8}$, in good agreement with the accepted molecular diameter. Since the function Σc_a is additive, the diameter of a molecule must be less than one-tenth of the distance of separation of the molecules in the liquid state, and the average diameter of the atom in a complex molecule like ether is so small as to suggest that atoms contract on combining to form a molecule. F. S.

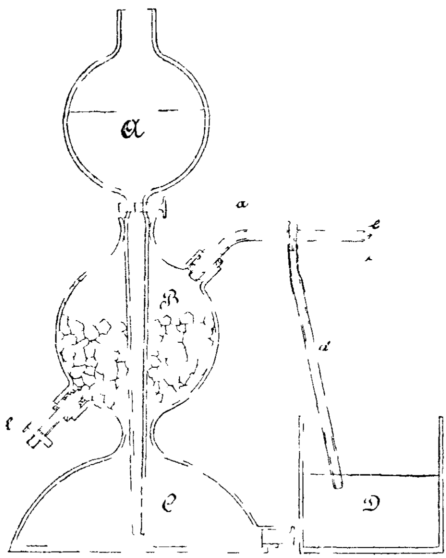
Distinction between and Knowledge of the Different Kinds of Isomerism. A. FOCK (*Ber.*, 1910, **43**, 1318).—The author considers that his views on isomerism (this vol., ii, 23) are in agreement with those of Kruyt (this vol., ii, 287), and not in contradistinction to them. T. S. P.

Brownian Movement and the Real Existence of Molecules. JEAN PERRIN (*Kolloidchemische Beihefte*, 1910, **1**, 221—300).—The paper gives a summary of work which, in part, has been already published (compare Abstr., 1908, ii, 927). The chief conclusion at which the author arrives is that the Brownian movement of colloidal suspensions and the movement of molecules are of the same type, and are due to the action of the same forces. The fact that molecular magnitudes calculated from observations on the Brownian movement are in agreement with the values obtained by the generally recognised methods is regarded as affording evidence in favour of the real existence of molecules. H. M. D.

Gas-Filling Apparatus for Lecture Purposes. WOLFGANG LENHARD (*Chem. Zeit.*, 1910, **34**, 471).—A convenient apparatus for filling cylinders by displacement with injurious gases, whether heavier or lighter than air. L. DE K.

Improved Kipp Apparatus. LEO GUTMANN (*Zeitsch. angew. Chem.*, 1910, **23**, 728—729).—The apparatus (see Fig.) differs from the original Kipp apparatus by being furnished with stopcocks, *a* and *b*, also with a three-way cock, *c*, in connexion with a tube, *d*, dipping into the water contained in the vessel, *D*. As soon as the acid in *B*

is spent, *a* is turned so that no more acid can enter from *A*, the communication with the wash-bottle is interrupted at *e* without altering the position of stopcock *c*, *b* is opened, and the spent acid is drawn off. *b* is then again closed, the communication with the wash-bottle is restored, and, after opening *a*, fresh acid is poured into *A*.



In order to prevent the mixing of the almost fresh acid in *A* with the partly exhausted acid in *C*, the stopcock *a* (when the apparatus is not being used) is closed, while stopcock *c* is opened in the direction towards *D*. The tube *d* and the water in *D* serve to carry off and absorb any hydrogen sulphide evolved. Later, the tube *d* is taken out of the water to prevent regurgitation of water into *B*. L. DE K.

Extraction Apparatus. NORMAN ROBERTS (*Amer. Chem. J.*, 1910, **43**, 418—424).—An apparatus is described which consists of a series of extractors, placed either vertically one below another, or arranged obliquely, each somewhat lower than that preceding it. Each extractor consists of an outer vessel containing an inner vessel, provided with a gauze bottom, in which is placed the material for extraction. The liquid after passing through the inner vessel accumulates in the outer vessel, from which it passes by a side-arm to the inner vessel of the next extractor of the series. In this way, the solvent, after circulating through each extractor of the series, reaches the boiling apparatus, in which the solvent is distilled off and the extract accumulates. The vapour of the solvent passes through a condenser, which returns the liquid to the first extractor of the series. This apparatus and suitable supports are described in detail with the aid of diagrams. It has been found useful for the extraction of maize meal with ether. E. G.

A New Form of Hot Filtering Apparatus. VIKTOR BRUDNY (*Zeitsch. wiss. Mikroskopie*, 1910, **26**, 418—421).—A form of hot-water funnel designed for employment in biological laboratories, as being capable of regulation through a wide range of temperature; it enables broths and agars to be filtered at their most suitable consis-

tency. It can be heated by electricity, or high boiling liquids such as glycerol or paraffin wax can be employed. A sketch with full details is given in the original. F. M. G. M.

Inorganic Chemistry.

Behaviour of Water at High Pressures and Low Temperatures. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1910, **72**, 609—631. Compare *Krystallisieren und Schmelzen*, Leipzig, 1903; Abstr., 1909, ii, 878).—The regions within which the different forms of ice can be realised are more accurately defined, and a new unstable form of ice, ice IV, is described.

Ice II and ice III have been prepared, and the pressures observed during the transformation of the forms into ordinary ice (ice I), and the corresponding temperatures have been determined. The curve which divides the region within which ice III cannot exist from that in which it can be realised, the so-called realisation-curve, coincides with that for ice II. This may be taken as indicating that the process of transformation of ice II into ice I is essentially the same as that of ice III into ice I, and it probably consists in the formation of double molecules from the single molecules of which ice II and ice III presumably consist.

The spontaneous crystallisation of ice I and ice III has been investigated. It was found that up to pressures of 2500 kilograms ice I invariably results from the spontaneous crystallisation of water. Even in the ice III region, the spontaneous crystallisation of ice I occurs more readily than that of ice III up to 2500 kilograms. Above the latter pressure, ice III forms, and as it has a smaller volume than the water from which it is formed, a vessel in which the pressure is greater than 2500 kilograms will not serve to demonstrate the expansive force of ice.

Two series of measurements were made of the temperatures and corresponding pressures at which ice which has spontaneously crystallised under high pressures begins to melt. In the course of the experiments, observations were made indicating that in some cases water spontaneously crystallises to a new unstable form of ice, ice IV, closely allied to ordinary ice, and readily changing into the latter. It was obtained most satisfactorily by cooling water very slowly in a dilatometer until it begins to crystallise between $-5°$ and $-7°$; it is then completely solidified by cooling to $-15°$, and then the temperature is slowly raised. In some cases the increase of volume is regular up to the melting point, indicating that only ice I is present; in other cases there is a marked expansion before melting, corresponding with the transformation of ice IV to ice I. G. S.

Behaviour of Chlorates, Perchlorates, Iodates, and Bromates towards Reducing Agents. DIOSCORIDE VITALI (*Atti Soc. Ital. Progr. Sci. Padova*, September 1909; *Giorn. Farm. Chim.*, 1910, **59**, 18—19. Compare Venditori, Abstr., 1908, ii, 63).—The reducing agents employed by the author are hydrogen sulphide, ammonium sulphide, hydrazine sulphate, ferrous ammonium sulphate, sulphurous and nitrous acids, zinc in presence of potassium hydroxide or dilute sulphuric acid, phosphorous, hypophosphorous and oxalic acids, aluminium and sulphuric acid diluted with an equal volume of water, iron and dilute sulphuric acid, and formic acid. In general, chlorates and perchlorates behave differently towards these reagents, the former being reduced, and the latter either undergoing no change or being very slightly reduced. In some cases this difference in behaviour is so marked as to allow of the detection of traces of a chlorate in a perchlorate. On the other hand, both iodates and periodates are reduced by the same reducing agents, both kinds of salt undergoing no change in some few cases. Bromates are also reduced by the above reducing agents. T. H. P.

Ultra-microscopy of Iodine Solutions. J. AMANN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 235—238).—Solutions of iodine in different solvents have been examined by means of the ultra-microscope. The violet solutions in carbon disulphide, chloroform, and carbon tetrachloride, and the yellowish-brown solutions in aniline, dimethylaniline, and phenol, are devoid of ultra-microscopic particles. Large numbers of particles are present in the brown solutions yielded by ethyl alcohol, methyl alcohol, acetone, glycerol, turpentine, amyl alcohol, terebenthene, and aqueous sodium iodide, and also in the violet solutions given by various petroleums. Benzene, toluene, xylene, acetic acid, ethyl acetate, propyl alcohol, water, and hydrogen peroxide give solutions which contain relatively few particles.

It has been found that the ultra-microscopic character of some of these solutions is completely changed when they are subjected to the influence of yellow or white light. The solutions in benzene, toluene, and xylene are specially photo-sensitive, and clouds of ultra-microscopic particles are rapidly formed when such solutions are illuminated by white light. This change is accompanied by a change in colour, the solutions assuming a brownish tint. When the light is removed, the brown solutions return to their original violet-red colour, and the ultra-microscopic particles disappear. In some other cases in which light causes the formation of colloidal particles there is no obvious change in the colour of the solutions. In consequence of the adsorption of the colloidal particles by the glass of the containing vessel, the ultra-microscopic particles disappear in many cases after a time, and optically clear solutions are obtained. H. M. D.

Elastic Sulphur Resembling Caoutchouc. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 250—251; *J. Russ. Phys. Chem. Soc.* (Phys. part), 1910, **42**, 159—160).—When molten sulphur is poured in a thin stream into liquid air, a fibrous form of sulphur is obtained, which possesses remarkably well-developed elastic properties. This elastic condition is transitory, and after about half an hour the

transparent fibrous sulphur becomes cloudy and changes into plastic sulphur. After twenty-four hours, the plasticity disappears and the sulphur becomes non-transparent and brittle. H. M. D.

Constitution of Dithionates and Sulphites. HENRI BAUBIGNY (*Compt. rend.*, 1910, **150**, 973—976. Compare this vol., ii, 125).—The formation of dithionates on heating silver sulphite or silver sodium sulphite shows that dithionic acid is composed of two sulphoxyl radicles, $(SO_3H)_2$, and lends no support to the formula, $SO_2{\cdot}OH$, suggested by Kolbe (1879). The reconversion of sodium dithionate into sodium sulphite by the action of metallic sodium (Spring, 1874) favours the unsymmetrical formula for the sulphites, $M{\cdot}SO_2{\cdot}OM$, suggested by Odling, and thus falls into line with the evidence adduced by Strecker, Schwicker, and others. R. J. C.

Tellurium. I. The Mutual Behaviour of the Elements Sulphur and Tellurium. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **12**, 602—617).—With the object of deciding the question as to whether sulphur and tellurium enter into combination, the author has investigated the nature of the cooling curves for mixtures of sulphur and carefully purified tellurium. The graphic representation of the freezing-point data indicates that there is no definite compound formed, but that the elements yield two series of mixed crystals of different crystalline form. The freezing-point diagram is similar to that which has been frequently observed with isodimorphous substances. The eutectic temperature is 106°.

The behaviour of tellurium towards the sulphides of the alkali and alkaline-earth metals is closely analogous to that of selenium and sulphur. Compounds containing tellurium and sulphur are obtained, and these may be regarded as derived from the polysulphides by partial replacement of the sulphur by tellurium. A barium compound, the composition of which agreed closely with the formula BaS_7Te_2, was obtained in well-formed, large, yellow, transparent, triclinic-pinacoidal crystals [$a:b:c = 1{\cdot}6835:1:1{\cdot}5515$; $\alpha = 113°7\frac{1}{2}'$, $\beta = 124°13'$, $\gamma = 77°39'$].

Basic tellurium nitrate, $Te_2O_3(OH)NO_3$, forms rhombic-bipyramidal crystals [$a:b:c = 0{\cdot}590:1:0{\cdot}607$]. H. M. D.

Preparation of Anhydrous Nitrates by Double Decomposition. ANTOINE GUNTZ and F. MARTIN (*Bull. Soc. chim.*, 1910, [iv], **7**, 313—326).—It has been shown already (Abstr., 1909, ii, 1019) that anhydrous metallic nitrates may be prepared by the action of nitric anhydride on the corresponding hydrated nitrates. An attempt has now been made to prepare anhydrous nitrates by the action of finely divided metals on silver nitrate in presence of ionising dry solvents, such as acetone, benzonitrile, or liquefied ammonia, and additive compounds obtained in these reactions are described.

Reduced copper in powder reacts with silver nitrate in presence of acetone, giving a blue solution, which on evaporation becomes viscous, evolves nitrous fumes, and finally explodes. If, however, the

solution, concentrated to contain 30% acetone, is poured into dry ether and the mixture cooled, *blue crystals*, m. p. $-28°$, are deposited; this material, when exposed under reduced pressure, is converted into a pale blue *powder*, m. p. 115°, of the formula $5Cu(NO_3)_2,4COMe_2$. Manganese behaves in like manner, but no definite compound could be isolated. Reduced iron and aluminium powder do not react in this way. A similar reaction takes place in benzonitrile, but in this case the additive compounds can be isolated by evaporation. The *manganese nitrate* compound, $2Mn(NO_3)_2,PhCN$, is a pale brown, crystalline mass, which melts and partially decomposes at 120°, and at 150° evolves nitrous fumes and leaves manganese oxide. Water dissolves and partly decomposes it. The *copper nitrate product*,
$$4Cu(NO_3)_2,PhCN,$$
is a green powder, which decomposes at 150°. Aluminium and iron do not react in this way.

In using liquefied ammonia, the reacting substances are placed in a tube, and ammonia is condensed on them by means of a freezing mixture. The tube is then placed in a steel cylinder, and set aside until the reaction is complete. More liquefied ammonia is added, and the solution obtained allowed to evaporate spontaneously, special precautions being taken to avoid the admission of moisture. In all cases the ammoniacal compound of the nitrate crystallises spontaneously from solution in liquefied ammonia. The following *products* were prepared: $Mn(NO_3)_2,9NH_3$, colourless crystals, becoming brown in air and light; $Ni(NO_3)_2,9NH_3$, pale violet crystals;
$$Co(NO_3)_2,9NH_3,$$
orange-red spangles; and $Cu(NO_3)_2,7NH_3$, small, blue crystals, which, under reduced pressure and in presence of sulphuric acid, pass into the compound $Cu(NO_3)_2,4NH_3$, which forms pale blue crystals with a violet tinge, and is probably identical with Kane's product (*Ann. Chim. Phys.*, 1839, **72**, 273). Horn's compound (Abstr., 1908, i, 121) could not be obtained. All these products are decomposed by water with the formation of metallic hydroxides; they evolve ammonia when exposed under reduced pressure or when heated slowly, although they all evolve nitrous fumes before losing all their ammonia. When rapidly heated they decompose, in some cases explosively.

With iron, no homogeneous ammoniacal compound could be prepared. T. A. H.

Monoperphosphoric Acid and Perphosphoric Acid. JULIUS SCHMIDLIN and PAUL MASSINI (*Ber.*, 1910, **43**, 1162—1171).—Electrolysis of solutions of phosphoric acid and its salts does not give rise to perphosphoric acid, neither does orthophosphoric acid react with hydrogen peroxide. When, however, phosphoric oxide or meta- or pyro-phosphoric acid is treated at low temperatures with 30% or stronger hydrogen peroxide and the reaction mixture afterwards diluted with ice-water, a solution is obtained which has oxidising properties similar to those of Caro's acid. It will even oxidise manganous salts to permanganic acid in the cold, a reaction which is not shown by Caro's acid. The analysis of the per-acid thus obtained was carried out by determining the maximum amount of oxygen which a molecule of

phosphoric acid could combine with; the excess of hydrogen peroxide was determined by titration with permanganate, and the amount of per-acid formed by measuring the iodine liberated immediately from potassium iodide. The results point to the formula H_3PO_5 or

$$PO(OH)_2 \cdot O \cdot OH,$$

the monoperphosphoric acid thus being derived from orthophosphoric acid no matter whether phosphoric oxide or meta- or pyro-phosphoric acid is used in the preparation.

Neither salts nor a benzoyl derivative (compare Abstr., 1909, ii, 566) could be isolated; the solutions decompose on concentration, although fairly stable when dilute. In the change from the per-acid to orthophosphoric acid there is no change in basicity, as is the case with Caro's acid. Acid solutions give no precipitates with salts of the heavy metals; neutral solutions give precipitates of the salts of monoperphosphoric acid, but they rapidly change to the ordinary phosphates with evolution of ozonised oxygen.

When hydrogen peroxide is treated with a large excess of pyrophosphoric acid, a perphosphoric acid of the composition $H_4P_2O_8$ is formed in small quantity in addition to monoperphosphoric acid.

Electrolysis of a dilute solution of phosphoric acid containing hydrogen peroxide gives rise to monoperphosphoric acid at the anode; this oxidation probably depends on the formation of perhydroxyl anions, HOO′.

Perphosphoric acid is not produced when ozone is led over phosphoric oxide. When, however, ozone is led over sulphur trioxide or through a solution of fuming sulphuric acid, persulphuric acids are formed. The monohydrate of sulphuric acid and ozone does not give rise to persulphuric acid.

A pernitric acid is not formed by the interaction of hydrogen peroxide and nitrogen peroxide. The pernitrous acid discovered by Raschig (Abstr., 1908, ii, 30) does not oxidise manganous salts, so that the authors consider it to be a hydroperoxide ester of nitrous acid, O:N·O·OH, and not a true per-acid. Its great instability is accounted for by its ready transformation into nitric acid. T. S. P.

Compounds of Sulphur and Phosphorus. VII. Phosphorus Pentasulphide, P_4S_{10} (P_2S_5). Alfred Stock [with Berla Herscovici] (*Ber.*, 1910, **43**, 1223—1228).—A mixture of 100 parts of purified red phosphorus with 260 parts of sulphur (2P : 5S, with 1% excess of sulphur) is heated to the distillation point, as described in the preparation of tetraphosphorus trisulphide (this vol., ii, 200). The finely powdered product is then heated in an evacuated sealed tube for several hours at 700°, and the resulting mass recrystallised several times from carbon disulphide; the crystals are finally dried at 100° in a current of hydrogen.

Phosphorus pentasulphide forms light yellow crystals, which sinter at 286—288°, m. p. 290°, and b. p. 513—515°/760 mm.; it has $D^{17} = 2{\cdot}09$, and is soluble in carbon disulphide to the extent of 1 part in 450 at room temperature, 1 : 550 at 0°, and 1 : 1200 at −20°. The molecular weight in carbon disulphide solution varies from 415 to 436, so that the molecular formula is P_4S_{10}. At 600° the vapour density

corresponds with the formula P_2S_5; at higher temperatures dissociation takes place (compare Abstr., 1908, ii, 274). T. S. P.

Colloidal Boron. F. 'AGENO and E. BARZETTI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 381—382).—By treating powdered amorphous boron, obtained by heating boric anhydride with powdered magnesium, repeatedly with water and decanting the latter, a reddish-brown colloidal solution of boron is obtained, which may be kept for some months without change. Faint traces of an electrolyte suffice to bring about rapid and complete precipitation of the boron, whilst hydrogen peroxide is decomposed by collöidal boron, which at the same time undergoes oxidation to boric acid. The colloidal solution possesses a very high resistance, and when it is electrolysed, the positive electrode becomes coated with a thin layer of amorphous boron, whilst the negative one remains clean; colloidal boron is hence electrically negative. T. H. P.

History of Colloidal Silicic Acid. PAUL WALDEN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 233—235).—The author recalls the fact that the solubility relationships connected with the colloidal nature of silicic acid were systematically investigated by Bergman in 1779. Quotations are given from Bergman's paper. H. M. D.

Alkali and Alkali-earth Amalgams. GEORGE McP. SMITH and H. C. BENNETT (*J. Amer. Chem. Soc.*, 1910, **32**, 622—626).—In the earlier paper (Abstr., 1909, ii, 663) it was pointed out that in the electrolytic preparation of the alkali and alkali-earth amalgams, the crystals obtained on filtration often contain a higher proportion of the alkali metal than that obtained by Kerp and Böttger (Abstr., 1900, ii, 656). The work of these authors has therefore been repeated, the mother liquor left on filtration being removed by means of a centrifugal machine. The results of these experiments indicate the existence of the compounds: $CsHg_{12}$, $RbHg_{12}$, KHg_{12}, $NaHg_5$, $LiHg_3$, $BaHg_{12}$, and $SrHg_{12}$. Of these indications, however, only those for the sodium and lithium compounds can be regarded as trustworthy, whilst the others merely prove that, in the general formula MHg_n, the maximum value of n is 12. By means of determinations of the specific volumes of amalgams of varying composition, Maey (Abstr., 1899, ii, 547) deduced the existence of $LiHg_5$, $LiHg_3$, and other compounds richer in lithium, but failed to obtain evidence of a sodium amalgam of higher mercury content than $NaHg_5$. The existence of the compound $NaHg_6$, described by Kerp and Böttger (*loc. cit.*), is very doubtful.

Although mercury itself will not adhere to such metals as platinum and iron, even very dilute alkali and alkali-earth amalgams readily do so. This is shown to be probably due to the inferior cohesion of the amalgams rather than to any chemical reaction. E. G.

Solubility of Potassium Iodide in Methyl Alcohol. MIECZYSLAW CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1910, **72**, 431—438).—The complete solubility curve of potassium iodide in methyl alcohol up to the critical temperature of the solution has been determined by

Alexéeff's method, the sealed tubes being half filled with the mixture. The maximum solubility occurs at 192°, the solution containing 29·6 grams of the salt in 100 grams; the solubility at the critical temperature, 266°, is about 8·64 grams in 100 grams. The temperature-coefficient of the solubility attains its maximum between 25° and 80°, and diminishes up to 192°, when it becomes zero. The temperature at which the boundary between liquid and vapour disappears on heating in the presence of excess of potassium iodide depends on the extent to which the tubes are filled; it gradually rises from 243·4° to 266·6°, when the solution in the tubes is increased from 15% to 46% of their volume, but falls to 263·9° when the tube is 50% full.

The effect of a number of other inorganic salts in raising the critical temperature of methyl alcohol and their solubility at the critical point, in grams per 100 c.c. of solution, have been determined with the following results: potassium chloride, elevation 0°, solubility zero; sodium chloride, 1·2°, 0·1%; potassium bromide, 1·2°, 0·2%; barium bromide, 0·7°, 0·4%; sodium bromide, 5·0°, 0·9%; mercuric chloride, 2·6°, 1·2%; cadmium chloride, 4·6°, 1·5%; potassium iodide, 2·6°, 8·6%. Mercuric bromide, mercuric iodide, and cadmium iodide are readily soluble at the critical temperature. G. S.

Transformations in Mixed Crystals of Sodium and Potassium Sulphates. Richard Nacken (*Centr. Min.*, 1910, 262—271. Compare Abstr., 1907, ii, 611).—The author's previous results are compared with those of Jänecke (Abstr., 1908, ii, 841) for the transformations in the same system. The arrests on the cooling curves are sharp, and do not indicate a transformation extending over a range of temperature in mixtures containing from 50 to 75 molecular % of potassium sulphate. It is probable that Jänecke's mixtures were insufficiently stirred, and did not reach complete equilibrium. The results are confirmed by microscopical examination, a mixture having the formula $Na_2SO_4,3K_2SO_4$ being perfectly homogeneous. C. H. D.

Technical Preparation of Borax. I. Mario G. Levi and S. Castellana (*Gazzetta*, 1910, **40**, i, 138—176. Compare *Gazzetta*, 1907, **37**, ii, 562).—The author's experiments deal with (1) the crystallisation of borax, and (2) the reaction between sodium chloride and boric acid. The results obtained in the latter part of the work are as follows.

The reaction between sodium chloride and boric acid does not take place below 140°, the velocity then increasing somewhat, in either absence or presence of superheated steam, and reaching a maximum at about 200°, corresponding with a yield of approximately 15% of borax; further rise of temperature, even up to 400° to 500°, is without influence on the extent to which the reaction proceeds. The reaction proceeds rapidly at a bright red heat, but is readily completed only at about 1000°; within these limits of temperature the velocity is increased about ten times by the presence of water vapour. Boric anhydride, obtained by the fusion of boric acid, reacts well at about 1000° with sodium chloride, the velocity being about the same as with orthoboric acid, and free chlorine being liberated. Anhydrous borax can be

heated to beyond its fusion point without undergoing any alteration in composition, but when it is fused in presence of water vapour, hydrolysis and abundant formation of boric acid take place.

The fact that the above reaction does not proceed appreciably below a temperature of 140° is undoubtedly connected with the formation of pyroboric acid, which, among the acids formed by the dehydration of orthoboric acid, is sufficiently fixed to displace hydrochloric and probably also other strong volatile acids (compare Mendini, *Boll. chim. farm.*, 1895, **34**, 705). T. H. P.

Action of Hydrogen Peroxide on Silver (Sub-)bromides. A. P. H. TRIVELLI (*Chem. Weekblad*, 1910, **7**, 351—353. Compare Trivelli, Abstr., 1909, ii, 455; and *Chem. Weekblad*, 1909, **6**, 525—530).—The author's contention that the reduction of photo-bromides by hydrogen peroxide cannot be explained by the composition $m\mathrm{Ag} + (n - m)\mathrm{AgBr}$, and that it accords with the formula $\mathrm{Ag}_n\mathrm{Br}_{n-m}$, since bromide is indifferent to hydrogen peroxide, was disputed by Luther, who considered that the reduction of the silver bromide might either be due to the presence of colloidal silver, or to the silver bromide being a component of an absorption compound with colloidal silver. The author considers that Luther's results do not invalidate the conclusions drawn by him from the results obtained in his former investigation.
A. J. W.

Ostwald's Law of Step-by-Step Transformation and the Photochemical Decomposition of Silver Halides. A. P. H. TRIVELLI (*Chem. Weekblad*, 1910, **7**, 404—406).—Ostwald's law supports the theory that the decomposition of silver halides into silver and halogen is attended by the intermediate production of silver sub-halides, and is opposed to the view that colloidal silver is formed directly from silver halides. These substances have the power of forming photochemical sub-halides only when in the solid state, and not in the liquid state, but silver halides in solution are reduced by chemical "developers" to sub-halides. The presence of alkali metal halides or ammonia induces reduction to metallic silver. The chemical "developer" may be regarded as a special solvent for the silver halide, the polymeric form of which goes into solution as a complex anion. Of the three sub-halides, the green variety is most sensitive to light, the red least, while the blue occupies an intermediate position. A. J. W.

Silver Antimonides. TH. LIEBISCH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 365—370).—Petrenko (Abstr., 1906, ii, 667) has shown that silver and antimony form the compound Ag_3Sb, and also that the saturated mixed crystals have a composition approximating to the formula Ag_6Sb. The author finds that the cooling curve of a fusion of a mixture of silver and antimony containing 84·38% of silver, which corresponds approximately with the formula Ag_6Sb, shows a break at 787°, and a second arrest at 556°. The resulting solid showed the presence of mixed crystals in a matrix of the compound Ag_3Sb. The mixed crystals have the same crystalline form as silver.

A specimen of regular silver antimonide from Andreasberg contained

83·90% Ag and 16·17% Sb, which corresponds approximately with the formula Ag_6Sb; D 10·05. The cooling curve of a fused sample was similar to that obtained with the synthetical Ag_6Sb, there being a break in the curve at 756° and an arrest at 556°.

Analysis of seven different samples of rhombic silver antimonide from Andreasberg gave percentages of silver varying from 74·41 to 75·86. This is slightly more silver than corresponds with the formula Ag_3Sb, which probably represented the original composition of the crystals, but owing to weathering the percentage of silver has increased.

T. S. P.

Action of Carbon Dioxide and of Air on Bleaching Powder. ROBERT L. TAYLOR (*J. Soc. Dyers*, 1910, **26**, 115—117).—In determining the action of carbon dioxide and of air on bleaching powder, the issuing gases are passed through an *N*/10-solution of sodium arsenite. This solution is then divided into two parts, one part being titrated with iodine and the chlorine in the other titrated with silver nitrate. The chlorine and hypochlorous acid are thus obtained, the equations being $As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl$ and $As_2O_3 + 2HOCl = As_2O_5 + 2HCl$.

Carbon dioxide acts on bleaching powder, either in the solid state or in solution, with liberation of chlorine only. The action is thus the same as that of sulphuric or nitric acid, and it is assumed that in this case, also, hydrochloric acid is liberated, decomposing the hypochlorous acid. Air, free from carbon dioxide, liberates only hypochlorous acid. If ordinary moist air, containing carbon dioxide, is used, both chlorine and hypochlorous acid are obtained, the proportion of the former continually increasing. C. H. D.

Dimorphism of Calcium Carbonate. HANS LEITMEIER (*Jahrb. Min.*, 1910, i, 49—74).—Solutions of calcium carbonate in carbonated water, to which different proportions of magnesium sulphate or chloride had been added, were kept in narrow-necked flasks for three months at temperatures of 2°, 10°, or 20°. At the lowest temperature only calcite was formed. At 10° and 20° there were deposited, together with crystals of calcite, curved rhombohodra of dolomite and minute, acicular crystals of aragonite. A larger proportion of aragonite was formed at the higher temperature and in solutions containing more of the magnesium salt. The presence of the magnesium salt has also a marked influence on the habit of the calcite crystals.

These results are discussed in connexion with the modes of occurrence of aragonite in nature. It is pointed out that mineral waters that deposit aragonite contain magnesium salts in solution.

L. J. S.

Calcium Silicides. OTTO HÖNIGSCHMID (*Zeitsch. anorg. Chem.*, 1910, **66**, 414—417).—The formulæ Ca_6Si_{10} and $Ca_{11}Si_{10}$, proposed by Kolb (this vol., ii, 35) for the products obtained by him, are inconsistent with the results obtained by the author (Abstr., 1909, ii, 808) and others. The reaction remained incomplete in Kolb's experiments, as the material was not completely fused, and indefinite

mixtures were obtained. Kolb's silicones and nitrides are also mixtures. C. H. D.

Permeability of Glass for Vapours. CONSTANTIN ZENGELIS (*Zeitsch. physikal. Chem.*, 1910, **72**, 425—430).—As Stock and Heinemann (Abstr., 1909, ii, 563) and Landolt (Abstr., 1909, ii, 1005) have been unable to confirm the author's statements as to the passage of vapours through glass (Abstr., 1909, ii, 134), the experiments have been repeated, and the earlier results confirmed. The objections of the above-mentioned authors, that the effect on the silver leaf might be due to coal-gas or to some impurity in the paraffin, are shown to be untenable.

An attempt was also made to detect a loss of weight when iodine or bromine is kept in sealed flasks, but the results were somewhat irregular. The weight of a sealed Erlenmeyer flask containing iodine diminished regularly, although very slightly, with time, but, except in one case, sealed distilling flasks containing the same substance showed no definite change of weight after keeping for three months. G. S.

Solubility of Magnesium Ammonium Sulphate. JOHN LOTHIAN (*Pharm. J.*, 1910, [iv], **30**, 546).—A re-determination of the solubility of crystallised magnesium ammonium sulphate; the results are much higher than those on record. The weight of the double salt dissolved by 100 grams of water is 18·22 at 1·1°; 20·72 at 5°; 22·48 at 10°; 24·08 at 15°; 24·81 at 15·5°; 28·26 at 20·5°, and 33·33 at 27·2°. L. DE K.

Thallous Selenate, Tl_2SeO_4. R. TH. GLAUSER (*Zeitsch. anorg. Chem.*, 1910, **66**, 437—438).—Thallous selenate may be prepared by fusing selenium with ten times its weight of thallous nitrate, or by heating the theoretical proportions of thallous nitrate and selenium dioxide. The salt melts above 400° to a yellow liquid, becoming white on cooling. C. H. D.

Special Bronzes. I. Lead Bronzes. FEDERICO GIOLITTI and M. MARANTONIO (*Gazzetta*, 1910, **40**, i, 51—77).—With a view to obtaining information concerning the structure of the lead bronzes containing about 10% of tin and 20% of lead, which are used largely for anti-friction purposes, the authors have investigated the ternary system copper–tin–lead, limiting themselves to alloys containing less than 20% of lead or 25% of tin.

Investigation of the binary system copper–lead shows that these metals form no definite compound, and that they are only incompletely miscible in the liquid state and not at all in the solid state; the eutectic point is practically coincident with the m. p. of lead.

In the ternary alloys, the tin is always present in the form of the copper compound, Cu_4Sn or Cu_3Sn, or a solid solution of these two. The results obtained with a number of alloys are fully discussed with the help of a space-diagram.

As regards hardness, this is not modified appreciably in alloys containing less than 14% of tin by the addition of lead in any proportion

less than about 10%. This result differs from that obtained by Guillet (Étude Industrielle des alliages métalliques), who stated that the hardness of these ternary alloys diminishes rapidly with increase of the lead-content when the latter exceeds 3%, but remains constant when more than 7% of lead is present; his investigations were, however, made on alloys containing also a small quantity of zinc, and were limited to 8·52—10·28% of tin. For alloys containing more than 14% of tin, especially when less than 5—6% of lead is present, the hardness decreases rapidly as the proportion of lead increases. This fact agrees with the microphotographic observation that in these alloys the free lead is almost entirely collected in, and diminishes the hardness of, the β-solid solution, to which the hardness is mainly due. T. H. P.

Formation of Double Salts. HARRY W. FOOTE (*J. Amer. Chem. Soc.*, 1910, **32**, 618—622).—An investigation has been undertaken with the object of ascertaining the influence of organic solvents on the formation of double salts which separate from water with water of crystallisation. The only work hitherto recorded on the formation of double salts from non-aqueous solutions is that of Cambi (Abstr., 1909, i, 412).

The salts selected for study were the double salts of mercuric chloride with sodium and potassium chlorides. Foote and Levy (Abstr., 1906, ii, 231) have shown that in water at 25° the following salts are formed: $NaCl,HgCl_2,2H_2O$; $2KCl,HgCl_2,H_2O$; $KCl,HgCl_2,H_2O$; and $KCl,2HgCl_2,2H_2O$. In the present experiments, alcohol was used as a solvent for sodium and mercuric chlorides, and both alcohol and acetone for potassium and mercuric chlorides. The solubility method was employed.

In the case of sodium and mercuric chlorides, a double salt is not formed at 25° from alcohol, and the conclusion is therefore drawn that water of crystallisation is essential to the combination of these salts.

The following double potassium mercuric chlorides were obtained: from alcohol, $5KCl,6HgCl_2,2C_2H_6O$; and from acetone,

$$KCl,5HgCl_2,C_3H_6O$$

and $5KCl,6HgCl_2,2C_3H_6O$.

These results indicate that when a double salt is formed containing the solvent, the latter is an essential constituent, and that the substitution of one solvent for another may prevent the formation of such a salt. E. G.

Magneto-chemical Analysis of Rare Earths. GEORGES URBAIN (*Compt. rend.*, 1910, **150**, 913—915. Compare Abstr., 1908, ii, 189). —The determination of the coefficient of magnetisation by means of Curie's magnetic balance affords a rapid and accurate method for following the progress of fractionation of rare earths. The composition of a mixture of two substances can be determined to within 2—3%; moreover, by repeating the determination on several successive fractions and comparing the results with the values calculated from the atomic weights, it is possible to detect the presence of minor

constituents; thus, the gradual accumulation of holmium was detected in the fractionation of a dysprosium-yttrium mixture.

W. O. W.

Action of Mercuric Chloride on Aluminium. ÉMILE KOHN-ABREST (*Bull. Soc. chim.*, 1910, [iv], 7, 283—286).—Thin films of mercury on aluminium foil behave as "inorganic ferments" in presence of water, giving rise to the formation of aluminium hydroxide.

Aluminium foil does not acquire a deposit of mercury when placed in a 0·0001% solution of mercuric chloride for six minutes; the deposition is hardly noticeable in a 0·001% solution in the same time, but it amounts to a few thousandths of the weight of the foil in a 0·01% solution, and rises to from 15 to 20% of its weight in a saturated solution of the perchloride.

Such amalgamated foil decomposes water when placed in it, forming aluminium hydroxide, and the rate of decomposition increases with (1) the concentration of the mercuric chloride solution used originally for the amalgamation of the foil, and (2) the duration of the immersion of the foil in the mercuric chloride solution. After the action on water is finished, the mercury is principally found mixed with the flocks of aluminium hydroxide lying on the surface of the foil, and is in a form (? oxide) soluble in hydrochloric acid, whence it is assumed that the mercury acts as a "ferment," being first oxidised by the water and then reduced by the aluminium.

T. A. H.

Nitrides and Oxides from Aluminium Heated in Air. ÉMILE KOHN-ABREST (*Compt. rend.*, 1910, **150**, 918—921. Compare Abstr., 1905, ii, 637).—Aluminium powder absorbs 8·8% of oxygen when heated at 600° in the air; on heating the resultant mixture in hydrogen chloride, the unaltered metal is removed in the form of a chloride, which is stated to contain 4% more aluminium than the trichloride, whilst the residual oxide contains less oxygen than is required by the formula Al_2O_3. When the heating is conducted at 800°, nitrogen and oxygen are absorbed simultaneously; on prolonged heating, however, the nitride undergoes oxidation. At 1100°, 22·5% of nitrogen is absorbed after ten minutes' heating.

When aluminium is heated at 900° in dry nitrogen, a grey substance is formed, containing more nitrogen than is required by the formula AlN; on heating the product in air, oxidation occurs, but the substance formed, although free from nitrogen, contains less oxygen than does alumina.

W. O. W.

Formulæ of Aluminium Salts and of the Corresponding Compounds of other Metals. G. H. COOPS (*Chem. Weekblad*, 1910, 7, 345—351).—By determining the elevations of the boiling point of alcohol produced by addition of amounts of aluminium chloride varying between 5·79% and 13·75%, the author has obtained as the molecular weight of aluminium chloride numbers varying between 243 and 382, the mean of six determinations with different concentrations being 271·3. He concludes that the molecular weight

is 267, corresponding with the formula Al_2Cl_6, and assumes that the aluminium atoms are united by a single linking. It was found impossible to prepare the ferric salts of monobasic acids in a state of sufficient purity to admit of the method being applied to them.

S. C. J. OLIVIER (*ibid.*, 378).—The author considers Coops's results untrustworthy, and atttributes them to the use of a hydrated aluminium chloride. He does not think that Coops has advanced any evidence in favour of the formula Al_2Cl_6. A. J. W.

Storage of Alum in Zinc Vessels. OTTO LANGKOPF (*Pharm. Zentr.-h.*, 1910, 51, 333—334).—Alum was stored for three months in a zinc vessel kept in a room in the tropics; the temperature varied between 30° and 39°. A white crust formed on the interior of the vessel, which was also eaten through in parts. The crust was partly soluble in water, the solution containing zinc and potassium sulphates; the residue was a mixture of a strongly basic aluminium sulphate with the oxides of aluminium and zinc.

The corrosion is explained as starting with the oxidation of the zinc at the high temperature of the tropics, the necessary water coming from the water of crystallisation of the alum. The zinc oxide then enters into further reaction with the alum. T. S. P.

Manufacture of Cementation Steel. IV. Specific Functions of Gaseous and Solid Cementation Agents. FEDERICO GIOLITTI and L. ASTORRI (*Gazzetta*, 1910, 40, i, 1—20. Compare Abstr., 1909, ii, 240).—Cementation of steel by means of mixtures of carbonic oxide and benzene vapour shows that small proportions of the hydrocarbon increase the concentration of the carbon in the outer zones of the steel beyond the value corresponding with the equilibrium between carbon monoxide and dioxide and carbon dissolved in γ-iron. This rise in the concentration of carbon increases with the proportion of benzene when the latter is small, but for larger proportions of benzene the velocity of decomposition exceeds that of solution; the carbon then forms a layer on the surface of the steel, and its concentration in the outside layer attains the value reached with solid cementation media; the concentration in this outer layer can be varied by altering the composition of the gaseous mixture.

Cementation by carbonic oxide and carbon together results in the addition of the separate actions. Also, when finely-powdered charcoal and steel almost free from carbon are brought into intimate contact at 1000° in a vacuum, the carbon dissolves, and in an atmosphere of nitrogen at 1000°, solid carbon produces cementation, which diminishes towards the interior of the steel.

Charpy's results (*Rev. de Métallurgie*, May, 1909) are criticised.

T. H. P.

Manufacture of Cementation Steel. V. Cementation with Strongly Compressed Gases. FEDERICO GIOLITTI and F. CARNEVALI (*Atti R. Accad. Sci. Torino*, 1910, 45, 337—345).—Further experi-

ments (compare *Gazzetta*, 1908, **38**, 309—351) show that in the process of cementation, the carburating gases play a direct part, and thus exert a preponderating action. T. H. P.

Cementation of Silicon Steels. LOUIS GRENET (*Compt. rend.*, 1910, **150**, 921—922).—Silicon steels which do not undergo cementation under ordinary conditions when heated in charcoal, readily do so when the operation is carried out with potassium ferrocyanide.
W. O. W.

The Behaviour of Goldschmidt's Ferroboron and Manganese-boron on Heating in Chlorine and Hydrogen Sulphide, and the Probable Chemical Nature of Borides. JOSEF HOFFMANN (*Zeitsch. anorg. Chem.*, 1910, **66**, 361—399).—The alloys of iron and manganese with boron, prepared by Goldschmidt's method, may be used for the preparation of boron sulphide, B_2S_3, by heating in a current of dry hydrogen sulphide. The sulphide is obtained in amorphous, white masses, glass, and crystals. The product is analysed by dissolving in hydrochloric acid in an atmosphere of carbon dioxide, and absorbing the hydrogen sulphide evolved in iodine solution. Boron is estimated by dissolving in water, adding potassium hydroxide, and evaporating, then neutralising with hydrochloric acid, boiling, and titrating with potassium hydroxide after the addition of glycerol. The results indicate that the compound B_2S_3,H_2S is mixed with the sulphide. Only about one-half of the boron in the ferroboron is converted, even after prolonged heating in hydrogen sulphide. Aqua regia extracts a boride having a composition approximating to Fe_3B_4, whilst the residue is richer in boron. Similar results are obtained with manganese-boron, the portion soluble in aqua regia approaching the composition MnB, whilst a greater residue is left than in the case of ferroboron.

When ferroboron is heated in chlorine, three products are obtained: a volatile liquid consisting of boron trichloride contaminated with iron compounds, iridescent green crystals of a *compound*, $3FeCl_2,BCl_3$, in the neighbourhood of the heated substance, and a red, rather more volatile substance, having the formula Fe_4BCl_{15}. Less residue remains than after the extraction with aqua regia.

Manganese-boron yields a volatile, yellow solid in small quantity, having the composition $2MnCl_2,BCl_3$. The residue appears to contain non-volatile chlorides.

The conclusion is drawn that borides prepared by Goldschmidt's method are mixtures of several different compounds. Formulæ for the double chlorides, in accordance with Werner's theory of complex compounds, are proposed. C. H. D.

Vanadium [in Steel]. GEORGE AUCHY (*J. Ind. Engin. Chem.*, 1909, **1**, 455).—See this vol., ii, 551.

Some New Double Arsenates. LOUIS J. CURTMAN (*J. Amer. Chem. Soc.*, 1910, **32**, 626—630).—If diammonium hydrogen arsenate is added to a hot solution of ferric chloride containing hydrochloric acid until a precipitate begins to form, and the mixture is then heated,

a white *ammonium ferric arsenate*, $(NH_4)H_2AsO_4,FeAsO_4$, is obtained, which is rapidly hydrolysed by water. This salt dissolves in ammonium hydroxide to form a deep reddish-brown solution, from which 95% alcohol precipitates a basic ammonium ferric arsenate.

When dipotassium hydrogen arsenate is used instead of the ammonium salt, a corresponding potassium ferric arsenate is produced. This compound and the double arsenates of aluminium and chromium are now being investigated. E. G.

Formation of Ultra-microscopic Gold Particles by the Action of Ultra-violet Light on Solutions of Gold Salts. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 238—240).—Experiments are described which show that ultra-violet rays have a considerable influence on the nature of the colloidal gold which is obtained by the action of reducing agents on solutions of gold salts. If a solution of chloroauric acid is made alkaline and reduced by means of hydrazine hydrochloride in the presence and absence of ultra-violet rays, the colloidal gold which is obtained consists of very much smaller particles in the former case. The change in the character of the solution which is brought about by the ultra-violet radiation disappears very slowly when the solution is kept in the dark before the reducing agent is added. Attention is called to the importance of these observations in connexion with photo-chemistry. H. M. D.

Mineralogical Chemistry.

A Natural Naphtha from the Province of Santa Clara, Cuba. CLIFFORD RICHARDSON and KENNETH GERARD MACKENZIE (*Amer. J. Sci.*, 1910, [iv], 29, 439—446).—The naphtha rises together with water and an emulsion of water, naphtha, and rhyolitic clay. It has been formed by the upward filtration of heavy petroleum through a stratum of clay, the light naphtha in the upper part of the stratum being subsequently liberated by the action of saline waters. The naphtha has $D^{15 \cdot 6}$ 0·732 and n_D^{25} 1·4092. Over one half distils between 100 and 125°, and very little above 150°. It is practically free from unsaturated hydrocarbons, and consists of nearly equal quantities of paraffins and naphthenes, the quantity of the latter being greatest in the fractions of highest boiling point. The oil obtained from the emulsion has the same composition, but has $D^{15 \cdot 6}$ 0·738. C. H. D.

The Wide Distribution of Scandium in the Earth. G. EBERHARD (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 404—426. Compare Abstr., 1908, ii, 862).—A further series of 459 samples of various minerals and rocks has been examined spectroscopically for

the presence of scandium, and traces or small quantities of this element were found in a large number of the samples. Although never present as an essential constituent, the largest amounts were found in æschynite and cassiterite from Embabaan in Swaziland, in monazite and wiikite from Impilaks in Finland, in wolframite from Sadisdorf in the Erzgebirge, and in cassiterite from Takayama in Japan. This element is almost constantly present in the minerals and rocks associated with tin ores, and it appears to be connected with the pneumatolytic or hydrothermal processes following the intrusion of granitic magmas. A special study was made of the minerals and rocks associated with the granite of the tin-mining district of Zinnwald in Bohémia. L. J. S.

Application of the Laws of Eutectics to Fused Silicates. FLAVIAN M. FLAWITZKY (*Nat. Phil. Soc. Imp. Univ. Kazan*, 1909). —The eutectic data given by Vogt (*Die Silikatschmelzlösungen*, II. 146, Christiania, 1904) for the pairs of minerals: augite (diopside) and olivine, augite (diopside) and ekermanite, melilite and olivine, and melilite and anorthite show that van't Hoff's formula for calculating the molecular depression of the freezing point is not applicable to the case of the silicates in their eutectic mixtures. The compositions of these eutectic mixtures and the depressions of the solidifying points of their components can, however, be determined with moderate accuracy by means of the laws developed by the author (compare Abstr., 1906, ii, 152). The results obtained indicate not, as was stated by Vogt (*loc. cit.*), that the molecules of the above silicates are not polymerised, but only that the degree of polymerisation is the same in each case. T. H. P.

Eutectic Structures in Silicate Fusions. MAX HAUKE (*Jahrb. Min.*, 1910, 91—114).—A modification is given of J. H. L. Vogt's formula for calculating the amounts of the components of eutectic mixtures from the data given by the melting point, the latent heat of fusion, and the molecular weight of each component. The calculated values for pairs of different rock-forming minerals are: 66·7 anorthite —33·3 olivine, 67 labradorite—33 olivine, 57 labradorite—43 diopside, 74 oligoclase—26 enstatite, 44 nepheline—56 diopside, 68 diopside—32 olivine. Some of these are in agreement with observed values, but there are a few discrepancies.

Mixtures of these pairs of minerals in the eutectic proportions given above were fused, either alone or in the presence of magnesium or calcium chloride or tungstic acid to act as mineralising agents. The crystallised products were examined under the microscope, and the structures observed are described in detail. In some instances the products consisted of the minerals that were fused together, whilst in others new components were formed. L. J. S.

The Arsenic Content of the Max Spring at Dürkheim a.d. Haardt. ERNST HINTZ (*Zeitsch. Balneol. Klimatol. Kurort Hyg.*, 1910, 3, Reprint 6 pp.).—The water from the Max Spring yielded 17·78 grams of dissolved mineral salts per 1000 grams, and of this the

comparatively large quantity of 0·01742 gram consisted of arsenic, calculated as trioxide.

The estimation was carried out by concentrating 2 litres of the water to a very small volume, which was then transferred to a distilling apparatus, the dish being rinsed with dilute hydrochloric acid. After adding a little ferrous chloride and excess of fuming hydrochloric acid, the arsenic was distilled off, and the distillate precipitated with hydrogen sulphide. The arsenious sulphide was then collected in a Gooch filter, washed first with water and then with alcohol and carbon disulphide, dried at 100°, and weighed. L. DE K.

Physiological Chemistry.

Control Tests of a Respiration Calorimeter. FRANCIS G. BENEDICT, J. A. RICHE, and L. E. EMMES (*Amer. J. Physiol.*, 1910, **26**, 1—14).—Electrical check experiments of the authors' calorimeter show that heat can be measured with an accuracy inside of 1% for periods as short as one hour. Check experiments in which alcohol was burnt in the chamber show that the measurements of heat eliminated, water vaporised, carbon dioxide produced, and oxygen consumed are in satisfactory agreement with the theoretical amounts. W. D. H.

A Comparison of the Direct and Indirect Determination of Oxygen Consumed by Man. FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1910, **26**, 15—25).—Further details introduced into the calorimeter to obviate error are described. Estimations of the oxygen consumed by the direct and indirect methods are in close agreement, but the direct method is preferable as the possible sources of error are less. No demonstrable quantities of nitrogen are eliminated as such. W. D. H.

The Causes of Absorption of Oxygen by the Lungs. C. GORDON DOUGLAS and JOHN S. HALDANE (*Proc. Roy. Soc.*, 1910, *B*, **82**, 331—333).—The authors admit the validity of Krogh's criticisms on the Haldane-Smith method, and renewed experiments on mice show that in ordinary circumstances diffusion alone will explain the entrance of oxygen into the blood. They, however, still hold that the secretory process is necessary as a supplementary process under certain conditions, for instance, when a high percentage of carbon monoxide is breathed. During rest the secretory process would be a waste of physiological effort, but during muscular work, when five or even ten times as much oxygen is absorbed, the blood would be incompletely saturated with oxygen if secretion did not occur. W. D. H.

The Influence of Increase of Alveolar Tension of Oxygen on the Respiratory Rate and the Volume of Air Respired while Breathing a Confined Volume of Air. THEODORE HOUGH (*Amer. J. Physiol.*, 1910, **26**, 156—168).—When a confined atmosphere

of about 30 litres containing an initial percentage of 60 to 80 of oxygen is breathed, the respiratory rate and minute volumes of air breathed are lower than with ordinary air, and there is laboured breathing from the very first. Increase of oxygen in the air modifies the respiratory condition of the tissues, if the behaviour of the respiratory centre is an indication of this condition. W. D. H.

The Mechanism of Gas Exchange. I. The Tensions of Gases in Arterial Blood. AUGUST KROGH and MARIE KROGH. **II. Oxygen Metabolism of the Blood.** A. KROGH. **III. The Gas Exchange in the Lungs of the Tortoise.** A. KROGH. **IV. The Combination of Hæmoglobin with Mixtures of Oxygen and Carbon Monoxide.** A. KROGH. **V. The Invasion of Oxygen and Carbon Monoxide into Water.** A. KROGH. **VI. The Rate of Diffusion of Carbon Monoxide into the Lungs of Man.** A. KROGH and M. KROGH. **VII. The Mechanism of Gas Exchange in the Lungs.** A. KROGH (*Skand. Arch. Physiol.*, 1910, **23**, 179—192, 193—199, 200—216, 217—223, 224—235, 236—247, 248—278).—This is a series of important papers dealing with the problem of preliminary respiration. Contrary to the views of Bohr and Haldane, and of the authors' expectations, no evidence was found of any secretory activity of the alveolar epithelium. The structure of these cells is highly favourable to diffusion of gases, and not adapted for secretory work. It is very different from that found in organs, such as the swim-bladder of fishes, where secretion of oxygen does occur. Indeed, in birds the alveolar epithelium is absent, and the endothelial cells of the capillaries alone have to be traversed by the gases. The experiments recorded in the first six papers are discussed and summarised in the last; so also are the views of the upholders of the secretory theory; these are shown to be untenable on both theoretical and experimental grounds. The general conclusion drawn is that the absorption of oxygen and the elimination of carbon dioxide in the lungs takes place by diffusion and by diffusion alone. There is no trustworthy evidence of any regulation of this process on the part of the organism.

The principal points in the argument may be best set out by dealing with the first six papers in order.

I. The authors' aerotonometer is an instrument of great precision for determining gas tensions in fluids. In rabbits, the blood passed through the instrument, and was returned to the circulation; it was kept fluid by the injection of hirudin. The tension of carbon dioxide in the arterial blood always closely follows that in the alveolar air; at any rate that in the blood is never more than 0·1% higher. The oxygen tension of the blood is always lower than that in the alveoli; the difference is generally 1 to 2%, in some cases 3 to 4% of an atmosphere.

II. This deals with the possible error in the tonometer, due to the using up of oxygen and the production of carbon dioxide in the blood itself. It was found that such metabolic processes do occur, involving the consumption of from 10 to 50 c.c. of oxygen per hour per kilo. of body-weight in rabbits at body temperature. Their intensity is there-

fore not sufficient to affect appreciably the tonometer determinations; in some of these experiments hirudin was omitted.

III. In the tortoise the vagus is a vaso-constrictor and not a gas-secretory nerve for the lung of the same side. Cutting it causes augmentation of the blood-flow through the lung. Here, also, the experiments lend no support to the theory of gas secretion, but prove that the exchange is due to mere diffusion.

IV. Here the carbon monoxide method of Haldane and Lorrain Smith is examined. The hæmoglobin of different animals does not necessarily possess the same relative affinity for oxygen and carbon monoxide. This being the case, the oxygen tension of the arterial blood of an animal cannot be deduced from the percentage saturation with carbon monoxide unless experiments are made *in vitro* with the blood of the same animal. Haldane and Smith constructed their curve from experiments on ox-blood; if their method is used and their basis of calculation be applied to the rabbit, the oxygen tension in the blood leaving the lungs works out at 34·5% of an atmosphere; if calculated from a curve derived from observations on rabbits' blood, it is 15%, which coincides with the tonometer reading.

V. The magnitude of the invasion-coefficient does not put any difficulty in the way of the diffusion hypothesis. It is obvious, on the other hand, that nothing can be said about the real conditions governing the absorption of gases in the lungs by diffusion merely from the invasion-coefficients. The oxygen has to be transported from the air, not only into the surface of the cells, but across them and the capillary endothelium into the blood. The tension-difference necessary to this end can only be determined by direct experiments on the living animal.

VI. Such experiments as those alluded to in the last sentence are here given. The necessary tension difference no doubt varies in different animals and even different people, owing to variations in the thickness of the epithelium and other factors, and it is shown here, as well as in the final paper (VII), that the actual tension differences which exist are sufficient for the end in view; for instance, the quantity of carbon dioxide eliminated during rest requires less than 1 mm. tension difference for its transport, and even in heavy work the mean tension difference cannot be more than 3 mm. The final tension difference between the blood and the alveolar air must therefore in any case be imperceptible. With reference to this gas, the experiments of Haldane and Priestley, which show the immediate effect on the respiratory centre of changes in the alveolar tension of carbon dioxide, support this view. The diffusion constants of the lungs and the mean tension differences between the blood and the alveolar air will also allow the necessary amount of oxygen to pass in. W. D. H.

Respiration of Bees during Spring, Summer, Autumn, and Winter. MARIE PARHON (*Bied. Zentr.*, 1910, **39**, 252—256; from *Ann. Sci. nat. Zoo.*, 1909, [ix], **9**, 1—57).—A colony of about six hundred bees was kept in a wire cage, and the respiration phenomena investigated by Pflüger and Colasanti's method. Respiration is extraordinarily vigorous. At 20° in summer time, 1 kilo. of bees

took in 17,336 c.c. of oxygen per hour and gave out 17,575 c.c. of carbon dioxide; flies only took in little more than one-third this quantity of oxygen, whilst other warm-blooded animals took much less. The respiration quotient for bees is 1·01, against 0·7 to 0·9 in other cases.

The relation between respiration and temperature varies with the season. In summer respiration increases as the temperature falls, until it reaches a maximum at 10°; in spring, autumn, and winter, however, the maximum is at 20°. These results are correlated with the average temperature to which the bees are accustomed during the seasons; thus in summer, when they were in the open air, they generally had a temperature of about 20°, and any fall in temperature was met by increased respiration. In autumn and winter the hive temperature was about 32—34°, and again a fall in temperature brought about increased respiration. The fact that the maximum occurs at so high a point as 20° indicates that bees are not particularly well able to accommodate themselves to low temperatures.

The respiration quotient does not change with the seasons, and is usually about 1, doubtless because the food supplied (honey) is mainly dextrose. The nitrogen supply comes from pollen, but the nitrogen content of bees does not appear to fluctuate during the year, neither does the glycogen content. E. J. R.

Adsorption by Blood. H. MORAWITZ (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 259—260).—Measurements have been made of the amount of mercuric chloride which is removed by blood-corpuscles from a sodium chloride solution of the mercury salt at 0°. The results agree with the view that the removal is an adsorption process. H. M. D.

The Relationship of Lipoids to Hæmolysis. WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1910, **62**, 258—265).—The influence of cholesterol, Merck's ovo-lecithin, kephalin, and cerebron on the hæmolysis produced by saponin, sodium oleate, sodium taurocholate, and cobra venom on sheep's and human blood-corpuscles was investigated. In all cases, cholesterol inhibited the process in varying degrees, and the same was proved to be true for the other lipoids investigated, and for the lipoid mixture obtained by extracting red corpuscles with alcohol. W. D. H.

Double Function of Calcium in the Coagulation of Blood and Lymph. HENRI STASSANO and A. DAUMAS (*Compt. rend.*, 1910, **150**, 937—939).—Calcium salts act in two directions in bringing about coagulation of blood and lymph. In traces they influence the two protein generators of fibrin-ferment, whilst in larger quantities they bring about formation of fibrin. The experimental evidence adduced in support of this conclusion was obtained from the study of a non-coagulating plasma containing 5% of sodium chloride, but freed from other salts by dialysis. Such a preparation does not coagulate on simple dilution. A portion was treated with a trace of a calcium salt, and several hours afterwards with a larger quantity of the same

substance, the addition of which brought about coagulation more rapidly than in another sample to which the salt had been added immediately after dilution. The optimum amount of calcium chloride required to effect the "internal work," rendered evident by the acceleration of clotting, was found to be 0·000021 gram per c.c. of plasma. It is supposed that this small amount induced the formation of fibrin-ferment, which, on the addition of larger quantities, acted on the fibrinogen producing the clot. The latter action was rendered evident by adding serum, freshly separated from the clot, to the serous, peritoneal liquid of a horse.

Under these conditions coagulation occurred, but was considerably accelerated by the addition of calcium chloride, and to a less degree by the chlorides of barium, strontium, potassium, and magnesium. The molecules of fibrinogen appear to become hydrated, under the influence of the salts, to the extent of becoming visible under the ultramicroscope. W. O. W.

The Existence of a Diastatic Enzyme in Leucocytes. LUDWIG HABERLANDT (*Pflüger's Archiv*, 1910, **132**, 175—204).—After the subcutaneous injection of starch grains in various warm- and cold-blooded animals, it is found that they are ingested by leucocytes, and are in great measure digested. Differences of detail are noted in different animals in relation to the kind of starch used; thus, in the mouse, potato starch is more resistant than wheat starch, and rice starch is the more resistant still. In the frog, rice starch is not digested at all. It is probable that the diastatic enzyme of serum first described by Bial is, in part, of leucocytic origin. W. D. H.

The Influence of Antipyretics on the Proteins of Blood-serum. CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1910, **62**, 357—364).—Antipyrin in moderate doses increases in normal dogs the proteins in the serum; the increase falls mainly on the globulin fraction, as the following table shows:

	Globulin.	Albumin.
Normal	1·752	3·105
After antipyrin	4·252	3·317
Increase	2·500	0·212

This is considered to be due to a diminution in metabolic processes in morphological elements, thus leading to an accumulation of unused protein in the blood. W. D. H.

Preparation by Electrical Dialysis of a Serium Almost Free from Electrolytes. CHARLES DHÉRÉ and GORGOLEWSKI (*Compt. rend.*, 1910, **150**, 993—996).—The authors give details for the preparation of a pure serum, from horses, by dialysis through collodion membranes aided by electrolysis. The method is capable of giving a serum having $K = 91 \times 10^{-6}$, comparable in its freedom from electrolytes with the solutions of colloidal metals prepared in an analogous manner by Whitney and Blake (Abstr., 1904, ii, 809). The serum obtained in this way is distinguished from an ordinary serum by the

ease with which coagulation is effected by alcohol, and by the fact that the solution becomes turbid at 44° and finally coagulates.

W. O. W.

The Physiological Permeability of Cells. III. The Permeability of the Salivary Glands to Sugar. Theory of Salivary Secretion. LEON ASHER and THEODOR KARAÚLOW (*Biochem. Zeitsch.*, 1910, **25**, 36—48).—The sugar content of venous blood is during secretion greater than that of the arterial. The greater the intensity of secretion the greater the difference. In the period of rest after activity, the venous blood, on the other hand, contains slightly less sugar than the arterial. On stimulating the resting gland to activity, sugar is set free from some unknown source, and serves as a source of energy for the act of secretion, and, owing to its greater permeability, diffuses into the blood. During rest the sugar is taken up again by the gland. The wall of the gland is permeable to sugar; no sugar, however, is found in the secretion, as the capacity for secreting sugar in the direction of the salivary secretion is wanting.

S. B. S.

Salivary Adaptation. JUDAH J. JONA (*Proc. physiol. Soc.*, 1910, xxi—xxii; *J. Physiol.*, **40**).—Chewing cane sugar produces a flow of saliva which contains invertase, an enzyme which is normally absent from saliva. This result is not, however, uniformly obtained in all people.

W. D. H.

The Relation of Ptyalin Concentration to the Diet and to the Rate of Secretion of Saliva. ANTON J. CARLSON and A. L. CRITTENDEN (*Amer. J. Physiol.*, 1910, **26**, 169—177).—In man, acetic acid is a more efficient stimulus to secretion than mechanical stimuli, as it probably affects more nerve-endings than a substance like dry sand. The concentration of the saliva increases with the rate of secretion; the saliva that is secreted most rapidly exhibits the greatest digestive power. The enzyme concentration in the gastric and pancreatic juices is quite independent of the secretion-rate. In all investigations on the influence of various diets, etc., on salivary activity, the secretion-rate factor must be recognised.

W. D. H.

Gastric Proteolysis. EUGÈNE CHOAY (*J. Pharm. Chim.*, 1910, [vii], 1, 335—341, 380—385).—A general method for the determination of the digestive power of proteolytic ferments is described. On the basis of the results obtained by the application of this method to the investigation of the action of gastric juice and pepsin on fibrin, the conclusion is drawn that the chief function of the gastric ferments is to render proteins soluble, the peptonising function being secondary, and that gastric juice is on the whole a more powerful hydrolytic agent than pepsin.

It is suggested that in examining proteolytic ferments, the following determinations should be made: (1) the weight of soluble matter produced by the digestion during six hours of a weighed quantity of the protein with a known quantity of the ferment in presence of

hydrochloric acid; (2) the change in optical rotation resulting from the digestion described under (1), and (3) the average molecular weight of the amino-acids formed during digestion. The last-mentioned determination is made by neutralising an aliquot part of the liquor resulting from the digestion, adding a neutral solution of formaldehyde, and then titrating with standard alkali, as suggested by Schiff. In the present experiments, dry pork fibrin (F), a dry extract (G) of the stomach membrane of the pig, and a commercial pepsin (P) were used. It was found necessary to introduce corrections for the soluble matter, rotation, and acidity of the initial mixtures of G or P with dilute hydrochloric acid.

The results obtained show that the dissolving power of G or P for F increases with the ratio F/G or P until this is equal to 50, and then diminishes, due apparently to a reversible reaction.

Diminution of specific rotation and lowering of molecular complexity in the digested product may be taken as a measure of the peptonising power of the ferments, and from the results obtained it appears that this is not very great for gastric juice or pepsin. The final specific rotation in both cases is of about the same value as that recorded by Adler for the protoalbumose of fibrin (*Inaug. Diss.*, Leipzig, 1907), whilst the average molecular weight is about the same as that of the octadecapeptide of Fischer. For the ratio F/G or $P = 50$, gastric juice has about the same activity as pepsin under similar conditions, but for ratios greater than this, gastric juice is the more active.

The results indicate that the action of gastric ferments in digestion is merely preparatory, and that the ultimate degradation to simple products is due to the action of the pancreatic juice. T. A. H.

Pancreatic Lipase. I. The Accelerating Action of Hæmolytic Substances and their Inhibition by Cholesterol. OTTO ROSENHEIM and J. A SHAW-MACKENZIE. **II. The Action of Serum on Pancreatic Lipase.** O. ROSENHEIM and J. A. SHAW-MACKENZIE. **III. The Separation of the Lipase from its Co-enzyme.** O. ROSENHEIM (*Proc. physiol. Soc.*, 1910, viii—xii, xii—xiii, xiv—xvi; *J. Physiol.*, 40).—I. Glycerol extracts of the pancreas prepared according to the authors' method are strongly lipoclastic. The accelerating effect of bile salts on lipase is a property shared by other hæmolytic agents; cholesterol also has a protective action both in hæmolysis and lipolysis.

II. Serum accelerates lipolysis, but human serum is comparatively inactive; in certain pathological conditions, however (cancer and other diseases also), the lipoclastic acceleration of the serum is increased, and this runs parallel with its antitryptic power. The accelerating substance in the serum dialyses, and is soluble in dilute alcohol: it is inhibited by cholesterol.

III. A glycerol extract of pancreas is inactive towards fats after filtration; the residue on the filter is also inactive; on mixing the two together, a mixture possessing the initial power of the extract is obtained. The same separation can be effected by the centrifuge. The activity of the filtrate is not diminished by boiling, but the potential energy of the residue is. Pancreatic lipase thus consists of

two inactive fractions; the substance in the filtrate, not destroyed by boiling, is termed the co-enzyme, and the deposit is termed inactive lipase; this may be obtained as a dry powder. The co-enzyme dialyses readily, and is soluble in dilute, but not in absolute, alcohol, or in ether. The inactive lipase is activated, not only by the co enzyme, but also by sodium cholalate and by glycero-phosphoric acid, but not by lecithin, choline, acids or alkalis. It is also activated by serum. The co-enzyme is probably produced in the pancreas and carried by the blood, and it may possibly play a rôle in enabling the tissue lipases to hydrolyse the fat carried to the tissues by the blood-stream. W. D. H.

Physiology of Movements and Digestion in the Intestine. ROBERT BAUMSTARK and OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 483—488).—The experiments were performed on a dog with a jejunal fistula on various diets. With fluid foods, the material passes through the fistula in a few minutes, but with solid foods the time is longer, and the pauses between the outpourings longer also. The cause of the regulation of intestinal movements, whether chemical or not, is discussed. W. D. H.

Gaseous Metabolism of the Small Intestine. I. The Gaseous Exchanges during the Absorption of Water and Dilute Salt Solutions. THOMAS GREGOR BRODIE and H. VOGT. **II. The Gaseous Exchanges during the Absorption of Witte's Peptone.** T. G. BRODIE, WINIFRED C. CULLIS, and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1910, **40**, 135—172, 173—189).—The small intestine of dogs was enclosed in an oncometer in order to study the rate of blood flow and the rate of absorption of the solution within the intestine. The blood-gases in the arterial blood and in the venous blood leaving the intestine were examined before the introduction of the solution, and at twenty, forty, and sixty minutes afterwards. The fluid remaining at the end of the hour within the intestine was also examined, and the intestine weighed.

The oxygen intake of the small intestine as a whole varies between 0·0056 and 0·0313 c.c. per gram per minute, with a mean of 0·0179 c.c. The carbon dioxide output varies between 0·0089 and 0·0321 c.c. per gram per minute, with a mean of 0·0199 c c. The respiratory quotient for the intestine at rest is 1·11. During the activity caused by making the intestine absorb distilled water and dilute salt solutions, the oxygen intake rises to 131% of the value at rest, and the carbon dioxide output falls to 94% of that at rest. In later stages the oxygen intake falls, but is still higher than at rest. At about thirty minutes after the commencement of absorption, the carbon dioxide output shows a marked fall to 69% of the rest value, even though the oxygen intake rises. The rate of blood flow rises to 139% of the rest value. The oxygen intake for the epithelial cells is higher than that of the intestine as a whole. It is estimated at 0·258 c.c. per gram per minute during rest, and 0·0368 at the height of activity, as compared with 0·0179 and 0·0234 for the intestine as a whole. The following are the corresponding figures for the carbon dioxide output, namely,

0·0318 (rest), 0·294 (activity), compared with 0·0199 (rest) and 0·0187 (activity) c.c. per gram per minute for the intestine as a whole.

In the experiments on the absorption of Witte's peptone, the total fluid remaining unabsorbed at the end of an hour was greater than in the case of salt solutions, and in the residual fluid the nitrogen concentration was increased. The mean oxygen intake in these experiments for the resting intestine was 0·0199, and the carbon dioxide output was 0·0175 c.c. per gram per minute; the CO_2/O_2 ratio was 0·87; the mean blood flow was 0·477 c.c. per minute. All these values rose during absorption to 160, 153, and 166% of the values at rest. The rate of nitrogen absorption varied from 7 to 10 milligrams per minute, and of fluid averaged 1 c.c. per minute. W. D. H.

The After Effect of Increased Muscular Work on Metabolism. A. JAQUET (*Arch. exp. Path. Pharm.*, 1910, **62**, 341—356).—Details of the gaseous interchanges in a man who did muscular work (mountain climbing) on one day are given, but most interest attaches to the examination of the urine, which showed a marked rise in the nitrogen excreted; the output per diem before the work averaged 16·24 grams; on the day of the work it rose to 19·23, and for four days after that was over 18·4. The diet was constant throughout; the sulphates excreted ran a parallel course. The chlorine and phosphorus showed a diminution on the work day, but rose again to the normal the next day. W. D. H.

Phosphorus Metabolism in Man. ÖSTEN HOLSTI (*Skand. Arch. Physiol.*, 1909, **23**, 143—153).—Experiments on animals in which the question has been investigated whether the body can obtain its phosphorus from inorganic sources have not in the hands of various investigators yielded concordant results. In the present experiments, in which organic and inorganic phosphorus were determined in the food and excretions of a man, the result obtained is that it is possible to supply the necessary phosphorus in large measure from inorganic phosphates. W. D. H.

Phosphorus Metabolism. IV. Phosphorus Excretion of a New-born Child. WOLFGANG HEUBNER (*Arch. exp. Path. Pharm.*, 1910, **62**, 252—257).—The amniotic fluid contained phosphorus only in traces; the distilled water in which the child had been bathed contained only 0·0007 gram. The urine passed during the first eight hours after birth contained 0·004 gram or 0·1% of the dry residue. From the ninth to the twenty-fourth hour, the child passed 29 c.c. of urine containing 0·005 gram. In the next nine hours, 31 c.c. were passed containing 0·00055 gram of phosphorus. The meconium was collected in two portions, which together yielded 0·0031 gram of phosphorus, or 0·04% of the dry residue. There was altogether an excretion of one-third of a milligram of phosphorus or three-quarters of a milligram of phosphoric acid per kilogram of body-weight in twenty-four hours. This probably represents the amount of phosphorus endogenously metabolised. W. D. H.

The Degradation of Fatty Acids in the Organism and the Mutual Relations of the "Acetone Substances." LEON BLUM (*Munch. Med. Wochenschrift*, 1910, Reprint).—The author has continued his work on this subject (compare Baer and Blum, this vol., ii, 227), the experimental method adopted in most cases being the subcutaneous injection of large quantities of the substance examined. When sodium acetoacetate is administered, *l*-β-hydroxybutyric acid is found in the urine; this is the case, not only with dogs, but also with normal and slightly diabetic human beings. When the degradation of butyric acid, hexoic acid, and *iso*valeric acid takes place in a normal animal, acetoacetic acid is first formed, and from this *l*-β-hydroxybutyric acid. The degradation of β-hydroxybutyric acid by way of acetoacetic acid seems to be due to disease of the liver cells; the amount of glycogen in the liver is not the only factor concerned. This decomposition is not effected in the normal animal. Liver after removal from the body can reduce sodium acetoacetate to *l*-β-hydroxybutyric acid. Crotonic acid is converted into β-hydroxybutyric acid in the body. *l*-β-Hydroxybutyric acid, unlike many other fatty acids, is only slightly toxic in its effects, so that the theory of diabetic coma which is based on its supposed toxicity is open to objection.

R. V. S.

Fate of the Amino-acids in the Organism. GRAHAM LUSK (*J. Amer. Chem. Soc.*, 1910, **32**, 671—680).—A review of recent work on the decompositions which proteins undergo in animal metabolism, particularly with reference to their "deamination" and conversion into fats or carbohydrates.

E G.

Is the Assimilation of Fat in the Body-cells Dependent on the Composition of the Fat in the Food? EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1910, **65**, 330—335).—The composition and physical constants of the body-fat of dogs does not vary with the kind of fat given; mutton fat and rape oil were the fats selected for the experiments.

W. D. H.

Fat Absorption. F. W. LAMB (*Proc. physiol. Soc.*, 1910, xxiii—xxvi; *J. Physiol.*, **40**).—Lorrain Smith and Mair's modification of Weigert's method is valuable for investigating the relative ease of oxidation of lipoid globules in the tissues. Fat absorption occurs in the stomach of kittens when fed on their mother's milk; the fat in the epithelium is readily oxidised, especially that in the gastric mucosa. The stomach fat shows an acid reaction to Nile-blue more readily than the intestinal fat. The rapidity with which fat reaches the stainable stage of the dichromate method, and the occurrence of anisotropic globules can be explained by the association of cholesterol. Saturated fat after absorption can be stained; this may be due to the presence of cholesterol or to a process of desaturation.

W. D. H.

The Digestion of Cellulose in Domesticated Animals. I. ARTHUR SCHEUNERT (*Berl. Tierarzt. Wochenschrift*, 1909, Reprint 4 pp.).—Historical. A critical account of the literature of the subject.

R. V. S.

The Digestion of Cellulose in Domesticated Animals. III. As to the Solubility of Cellulose in the Saliva of the Sheep. ARTHUR SCHEUNERT (*Berl. Tierärzt. Wochenschrift*, 1910, **26**, Reprint).—The author finds that cellulose remains unaffected after having been in contact with sheep's saliva for three days at body-temperature. This is also the case if the saliva is rendered faintly acid with acetic acid, and it follows, therefore, that under no circumstances can cellulose be digested in this way, although the contrary has been stated. R. V. S.

The Metabolism of Some Pyrimidine Derivatives. LAFAYETTE B. MENDEL and VICTOR C. MYERS (*Amer. J. Physiol.*, 1910, **26**, 77—105).—Cytosine and uracil intravenously introduced do not contribute to purines in the urine. The same is probably true for thymine, but the results are not so uniformly negative. Creatinine metabolism is also unaffected. These substances can be recovered unchanged in the urine both after feeding and injection; they are thus stable substances. On the other hand, pyrimidine substances cannot be detected in the urine after nucleic acid is given. They have no marked pharmacological or toxic properties. W. D. H.

The Action of Massage on Protein Metabolism. DODO RANCKEN (*Skand. Arch. Physiol.*, 1910, **23**, 279—294).—The small but variable increase of urinary nitrogen during massage noted by previous observers has received various explanations. The present experiments on man conducted with suitable precautions confirm the main fact of the increase, but it is so small that it cannot possess any physiological importance. W. D. H.

The Value of Protein Cleavage Products in the Animal Organism. XIII. EMIL ABDERHALDEN and FIDEL GLAMSER. **XIV.** E. ABDERHALDEN and DIMITRIE MANOLIU (*Zeitsch. physiol. Chem.*, 1910, **65**, 285—289, 336—349).—XIII. Particulars are given of experiments on two dogs; one received its protein in the form of digested milk, the other in the form partly of milk partly of flesh; fat and carbohydrate were given also. In both cases the nitrogen balance was negative.

XIV. In these experiments, dogs were fed on flesh, gelatin, the missing cleavage products of gelatin, and the necessary amount of carbohydrate and fat. The animals usually suffered from diarrhœa and sickness, and nitrogenous equilibrium was not maintained. Perhaps gelatin lacks certain constituents which are not yet recognised. W. D. H.

The Resorption of the Bence-Jones Protein. L. BORCHARDT and A. LIPPMAN (*Biochem. Zeitsch.*, 1910, **25**, 6—17).—The Bence-Jones protein was administered *per os* to dogs, which were killed a few hours afterwards. The blood was tested for the Bence-Jones protein (of human origin) both by purely chemical methods and by the precipitin reaction. In a few cases the protein could be detected by purely chemical methods, but in all by the precipitin reaction, and the

conclusion is drawn that the protein can be resorbed unchanged from the alimentary tract. No conclusions could be drawn as to the quantity thus entering the circulation. S. B. S.

Digestion of Connective Tissue. ROBERT BAUMSTARK and OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1910, **65**, 477—482).—Kühne and Ewald found that uncooked collagenous tissue is not digested by trypsin, but is by pepsin-hydrochloric acid; this was confirmed by A. Schmidt, who regarded the undigested material as ballast for the fæces. The present experiments were carried out *in vitro*, and these confirm the statements of Kühne and Ewald. Some experiments were also made *in vivo* in dogs with fistulæ. It was found that a considerable amount of digestion occurs in the duodenum, but this is attributed not to the pancreatic or duodenal juices, but to the continued action of pepsin-hydrochloric acid after it has passed the pylorus. W. D. H.

The Physiology of Cell Division. II. The Action of Isotonic Salt Solutions on Unfertilised Eggs of Asterias and Arbacia. RALPH S. LILLIE (*Amer. J. Physiol.*, 1910, **26**, 106—133). —Unfertilised eggs placed in pure solutions of neutral salts isotonic with sea-water undergo a loss of pigment, which is an effect analogous to hæmolysis, and indicates increased permeability of the plasma membrane; the relative effect of sodium salts is

$$NaCl < NaBr < NaNO_3 < NaCNS < NaI.$$

Potassium salts are more gradual in their action. After a short exposure to such solutions, the eggs when transferred to sea-water usually exhibit cleavage, and thus the view is supported that increase in the permeability of the membrane is the primary change in the initiation of cell division. W. D. H.

Action of the Choroid Plexuses on the Secretion of Cerebrospinal Fluid. WALTER E. DIXON and WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1910, xxx—xxxiii; *J. Physiol.*, **40**).—An extract of the choroid plexuses derived from ox, sheep, and man (1 gram of the dried material to 100 c.c. of normal saline solution) causes a secretion (in anæsthetised dogs) of the cerebro-spinal fluid. A similar excitation, but much less pronounced, is produced by extract of brain (dog, ox, sheep). Many other substances and extracts which were tried were without action. W. D. H.

The Gaseous Exchange of Nerve Fibres after Section. VITTORIO SCAFFIDI (*Biochem Zeitsch.*, 1910, **25**, 24—35).—The gaseous exchange was measured in the Thunberg-Winterstein microspirometer. The material employed was the sciatic nerve of frogs. The consumption of oxygen was in all cases measured. The gaseous exchange was measured in the nerve-fibres removed from animals at varying periods after the section. It was found that in the first few days after section there is an increase in the oxidative processes. The respiratory quotient both in the degenerating and normal nerves is always less than unity. S. B. S.

Chemical Excitation and Paralysis of Non-medullated Nerves and Smooth Muscle in Invertebrates. Investigations on the Chromatophores of Cephalopods. F. B. Hofmann (*Pflüger's Archiv*, 1910, **132**, 82—130).—Substances which stimulate nerve trunks (sodium hydroxide, triethylamine, ammonium sulphate, nicotine, physostigmine) produce on subcutaneous injection in cephalopods (especially in decapods) a stimulation of the cutaneous nerves. Those which paralyse (cocaine, chloral hydrate, etc.) neutralise the effect of mechanical and electrical stimuli. Some of these substances produce a local effect when applied to the skin. The question is discussed at length on what part of the neuro-muscular apparatus of the chromatophores the effects are due.

W. D. H.

Rôle of the Constituents of Dissociation of Tricalcium Carbophosphate in the Formation of Osseous Tissue and Various Concretions, Having as a Basis Calcium Phosphate and Calcium Carbonate. A. Barillé (*J. Pharm. Chim.*, 1910, [vii], 1, 342—348, 377—380).—The view already expressed (Abstr., 1909, ii, 324) that the formation of bone and of calculi and similar abnormal concretions in the organism is due to the dissociation of carbophosphates (Abstr., 1902, ii, 258; 1904, ii, 27) is supported by the results of a number of analyses of calculi given in detail in the original. In stating the results of analyses of calculi, the author converts all the bases present into their lime equivalents, then associates the necessary amount of lime with the acids other than phosphoric acid present, and finally assumes that the rest of the lime is combined with phosphoric acid, the ratio of these two making it possible to say whether dicalcium or tricalcium phosphate or a mixture of the two is present. It is also desirable to state whether or not the medium in which the calculus is found is acid or alkaline.

T. A. H.

Influence of Different Substances on the Gaseous Exchange of the Surviving Muscular Tissue of Frogs. III. Torsten Thunberg (*Skand. Archiv. Physiol.*, 1909, **23**, 154—161. Compare this vol., ii, 54).—In previous work it was shown that the chlorides of calcium, barium, and strontium lessen the gaseous interchange which occurs in surviving frog's muscle, whilst that of magnesium is comparatively inactive. The present research deals with the influence of hydrogen and hydroxyl ions. Dilute solutions of hydrochloric acid and various hydroxides were employed in equivalent concentrations; hydrochloric acid lessens the gaseous metabolism much more than sodium hydroxide; calcium hydroxide is more powerful than sodium hydroxide, and magnesium hydroxide more powerful still; in the latter case concentration of hydroxyl ions less than 7×10^{-4} lessens the uptake of oxygen to a third of the normal.

W. D. H.

Survival of an Excised Muscle Under Aseptic Conditions. George R. Mines (*Proc. physiol. Soc.*, 1910, xvii—xviii; *J. Physiol.*, **40**).—In sterile Ringer's solution, a frog's sartorius remained excitable for twenty-one days.

W. D. H.

The Effects of Distilled Water and of Various Solutions on the Weight and Length of Striated Muscle. EDWARD B. MEIGS (*Amer. J. Physiol.*, 1910, **26**, 191—210).—Striated muscle undergoes (as Overton stated) two kinds of swelling, one due to the presence of a membrane permeable to water, but not to salts and other crystalloids; the other is best studied after the destruction of the membrane, and is akin to the swelling observed in gelatin or fibrin in water, acids, and alkalis. This second kind is a property of the muscle sarcostyles alone. McDougall's main contention, that the contraction of striated muscle is the result of the swelling of the sarcostyles, and that this is produced by the formation within them of sarcolactic acid, is supported. W. D. H.

Action of Organic Acids on Muscle as a Function of Chemical Change. Action of Nicotine and Other Pyridine Bases on Muscle, and on the Antagonism of Nicotine by Curarine. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xviii—xx, xx—xxi; *Proc. Roy. Soc.*, 1910, *B*, **82**, 333—345).—The relative values of the organic acids are of a higher order as determined by the muscle method than by physico-chemical methods, but the relative position of the acids is the same except in the case of oxalic acid.

The toxic power of nicotine on muscle is about one-third of that of quinine, and six times greater than that of curarine. The characteristic effect of nicotine on muscle is not produced by pyridine, picoline, or piperidine, and these substances are all less toxic than nicotine. One molecule of curarine overpowers the effect of 100 of nicotine.

W. D. H.

Muscle Enzymes. FRED RANSOM (*J. Physiol.*, 1910, **40**, 1—16). —From frozen muscle a plasma can be prepared which contains enzymes capable of converting dextrose and glycogen into lactic acid, carbon dioxide, and alcohol. By alcohol-ether a precipitate is obtained which acts in the same way, but less rapidly.

W. D. H.

The Respiration of the Tortoise Heart in Relation to Functional Activity. HORACE M. VERNON (*J. Physiol.*, 1910, **40**, 295—316).—Oxygenated Ringer's solution maintains the vitality of the tortoise heart for one hundred and five hours. The force of the beat and the output of carbon dioxide gradually diminish, but the latter rises again with the onset of putrefaction in portions of the perfused heart. Tortoise serum and 0·1% dextrose do not improve the sustaining power of the solution, and the optimum concentration of potassium chloride is 0·02%. Mercuric chloride does not directly affect cardiac contractility, but sodium chloride and formaldehyde do; hearts poisoned over and over again with these drugs and also with hydrogen cyanide and sodium hydrogen sulphite show perfect recovery on once more perfusing with Ringer's fluid. W. D. H.

The Significance of Carbon Dioxide for the Heart Beat. E. JERUSALEM and ERNEST H. STARLING (*J. Physiol*, 1910, **40**, 279—294). —An increase in the carbon dioxide tension of the blood causes a

slowing and a relaxation of the heart; with high percentages this affects the systolic more than the diastolic volume, so that the ventricular output is lessened; with moderate tensions the output increases. There is a certain optimum tension which probably rises with fall of temperature of the blood. In acapnia, as pointed out by Henderson, the output is therefore minimal. W. D. H.

Action of Glucinum, Lanthanum, Yttrium, and Cerium on the Frog's Heart. GEORGE RALPH MINES (*J. Physiol.*, 1910, 40, 327—346).—Glucinum solutions have a powerful action on the frog's heart; this is due to their hydrolysis and consequent acidity. Salts of lanthanum, yttrium, and cerium are not hydrolysed, and produce effects similar to those caused by acid; they are antagonised by alkali. The hydrogen ion is more effective than the bi-valent ion, but less so than the ter-valent metallic ion in stopping the heart. The electrical charge is not the only important factor in the action of bi-valent ions (as is seen by the quite different actions of calcium and magnesium); it is, however, of overwhelming importance in the case of ter-valent ions. W. D. H.

Exhalation of Drugs by the Lungs. ARTHUR R. CUSHNY (*J. Physiol.*, 1910, 40, 17—27).—The exhalation of volatile substances (alcohol, acetone, anæsthetics, etc.) from the lungs is exactly analogous to their evaporation from water, the pulmonary cells being passive. The less the solubility in, and the more distant the affinity of a substance for, water, the larger is the amount exhaled. W. D. H.

Fatty Acid Metabolism in the Liver. I. V. H. MOTTRAM (*J. Physiol.*, 1910, 40, 122—134).—A method for the estimation of fatty acid requiring only 10 grams of liver is described in detail. It gives concordant results, which are higher than those obtained by Rosenfeld's method. In antiseptic and anaërobic autolysis, little or no alteration in the fatty acids of the liver was found either in amount or in the direction of desaturation. W. D. H.

Absorption of Sugar in the Kidneys. M. NISHI (*Arch. exp. Path. Pharm.*, 1910, 62, 329—340).—In the kidneys of rabbits and dogs, sugar is only present in the cortex; in hyperglycæmia this is increased. In glycosuria produced by diuretin and adrenaline, sugar is increased in the kidney, especially in the cortex, and it also occurs in the medullary region. In phloridzin diabetes the kidney contains less sugar than in other cases of glycosuria, and there is less in the cortex than in the medulla. In adrenaline hyperglycæmia without glycosuria, and sometimes in normal animals, a fluid which contains sugar can be forced out of the renal tubules by strong pressure. Rabbits' kidneys contain normally no glycogen, in hyperglycæmia without glycosuria a trace, and even in glycosuria a quite small amount. These results are interpreted as indicating that sugar is normally excreted in the glomeruli and absorbed in the tubules.

W. D. H.

The Internal Secretion of the Thyroid. ANTON J. CARLSON and A. WOELFEL (*Amer. J. Physiol.*, 1910, **26**, 32—67).—The lymph production of the normal thyroid is slight, but is increased when the gland is hypertrophied, or is the seat of a tumour. There is no relation between the amount of lymph and the iodine contained in the organ. The lymph, except that it contains fewer lymphocytes, has the characters of ordinary neck lymph. It contains no iodine, and Hunt's acetonitrile test gives negative results. The amount of iodine in dog's thyroid is very variable, and may be absent. The internal secretion of the thyroid and parathyroid probably enters the blood rather than the lymph. The thyroid may assume parathyroid structure and vice versa; both organs may perform their functions when both colloid and iodine are absent. W. D. H.

The Fat-splitting and Oxidising Ferments of the Thyroid Glands and the Influence of the Latter on Lipolytic and Oxidative Processes in the Blood. A. J. JUSCHTSCHENKO (*Biochem. Zeitsch.*, 1910, **25**, 49—78).—The lipolytic capacity of the thyroid glands is equal to that of the spleen and testicles, and inferior only to that of the liver and pancreas. The lipase acts chiefly on the butyrins, and to a less degree on natural fats. The thyroids of carnivora are more active in this respect than those of herbivora. On drying at a low temperature, the glands only lose to a slight extent their activity. The ferment is only extracted to a small extent by glycerol, but readily by water; it is destroyed on boiling. The removal of the thyroids in dogs causes a diminished lipolytic power of the serum, whereas hyperthyroidism increases it. The thyroids also contain a catalase, as do the red blood-corpuscles. The influence of thyroidectomy on the catalase content of the latter was investigated. In rabbits there was first an increase of oxidative energy, and then a diminution until the normal was attained. In dogs a decrease of oxidative energy was observed. No definite conclusions could be drawn as to the result of hyperthyroidism on this factor. S. B. S.

The Effect of Thyroidectomy on the Development of Active Immunity in Rabbits. C. A. FJELDSTAD (*Amer. J. Physiol.*, 1910, **26**, 72—76).—Thyroidectomy in rabbits does not during the first month affect the formation of immune substances. W. D. H.

Action of Extracts of the Anterior Lobe of the Pituitary on Blood-Pressure. WALTER W. HAMBURGER (*Amer. J. Physiol.*, 1910, **26**, 178—180).—Extracts of the anterior lobe of the pituitary cause lowering of the blood-pressure. The active substance is soluble in alcohol, glycerol, and salt solutions, but insoluble in ether. Previous treatment of the material with chloroform to prevent putrefaction inhibits the effect. W. D. H.

The Relationship of Aqueous Extracts which contain Nuclein Enzymes to the Physiological Phenomena in the Living Organisms. WALTER JONES (*Zeitsch. physiol. Chem.*, 1910, **65**, 383—388).—A discussion of the results obtained by the author and by others in relation to the question mentioned in the title.

W. D. H.

Pigment Formation. CARL NEUBERG (*Zeitsch. Krebsforschung*, 1909, **8**, Heft 2).—The origin of melanin, the black pigment of melanotic sarcoma, is still unknown; the presence or absence of iron is of small importance in its possible relationship to hæmoglobin, and in the absence of any guarantee of purity, the decomposition products stated to be obtained from it do not assist the solution of the problem. From a melanotic sarcoma of the adrenal body, an extract was obtained which contains an enzyme that coloured adrenaline and *p*-hydroxyphenylethylamine black, but had no effect on tyrosine; whether the pigment formed was the same as the natural one is quite uncertain. In other cases no active extract was obtained, and in one case recorded by Alberg (*J. Med. Research*, **16**, 117), the extract acted on catechol, but hardly at all on tyrosine. The main pigment, however, treated of in the present research is the black pigment of the *Sepia*. If the cleaned ink-bags of these animals are extracted with sea-water, in some few cases the extract colours adrenaline blackish-brown; in the majority of cases the extract has no such action.

Twelve grams of adrenaline were subjected to the action of an active extract, and 1·25 grams of a black precipitate were obtained, which contained C 60·64, H 5·2, N 7·07, and ash 0·32%; the presence of iron in the ash indicates how easily small amounts of this metal may creep in as an impurity. The extract had no action on a large number of organic substances; tryptophan alone yielded a similar but probably not identical product. Analysis of sepia-melanin itself yielded analytical figures very close to those given by Nencki and Sieber; some attempts were made to examine the action on it of nitric acid and other reagents, but although a nitro-derivative was obtained, no great stress is laid on this preliminary work. W. D. H.

The Ferments of Milk. JULIUS MEYER (*Arbeiten aus dem. Kaiserl. Gesundheitsamt*, 1910, **34**, 115—121, Reprint).—The author criticises an investigation on the Storch reaction of milk by Bordas and Touplain (Abstr., 1909, ii, 505) (blue colour said to be produced by the catalase of unboiled milk when treated with hydrogen peroxide and the hydrochloride of *p*-phenylenediamine), who believe that the reaction is due to the calcium caseinogen compound, which is precipitated, according to Duclaux, on boiling. The author shows that the Storch reaction does not occur (except after a long interval) in either the cream or the skimmed milk if the latter has been heated. Caseinogen, prepared by various methods, both from heated and unheated milk, was also incapable of yielding the Storch reaction. Milk-serum gave also a negative result. The author shows also that the property of decomposing hydrogen peroxide is not identical with that of yielding the Storch reaction, and draws the conclusion that there is no reason to disbelieve that the latter is due to a catalase.

S. B. S.

Coagulation of Fresh Milk by the Ferments of Boiled Milk. C. GERBER (*Compt. rend.*, 1910, **150**, 1202—1204).—Experiments on the time required by different ferments to coagulate milk after it has been heated for a definite time at different temperatures

(72—100°) show that there is a definite relationship between the presence of the globulins and albumins and the resistance of the milk to coagulation. The proteins are not strictly speaking anti-ferments, but appear to exercise a direct action on casein, protecting it from attack by the enzymes. W. O. W.

Isolation of Erythrodextrin from the Urine of a Dog. YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, 65, 414—416).—A dextrin-like substance in human urine has been described in two cases. The present observations on a dog gave the unique result of the presence of erythrodextrin in its urine. The dog had received a dose of 4 grams of hydroxyphenylglyoxylic acid by the mouth ; but a few months later, no effect was produced by the same dose, and other dogs also gave a negative result. W. D. H.

Pressor Bases in Urine. II. WILLIAM BAIN (*Lancet*, 1910, 1, 1190—1193).—The pressor bases which are present in the urine of normal adults can be most readily obtained by shaking the urine with Fleming's blood-charcoal and subsequently extracting the charcoal with suitable reagents. The urine of growing children contains the bases in minimal amount. In two adult cases the substitution of a milk and biscuit diet for one rich in meat made little or no difference in the amount of pressor bases in the urine. This suggests that they are formed in the lower intestine, where the growth of organisms is less restricted, owing to the removal of carbohydrates by absorption higher up. Medicinal doses of antiseptics by the mouth made no appreciable difference. In all cases of high blood-pressure the bases are absent or nearly so; this probably means that they are retained in the body. There seems to be no direct relationship between gout *per se* and the retention of the bases. In cases where the urine deposits uric acid there is marked diminution in the colloid matter of the urine; as the colloid contains chondroitin sulphuric acid, the association of this condition with urate deposition in cartilage is suggestive. W. D. H.

The Excretion of Morphine under the Influence of Intestinal Irritants. FRANCIS H. MCCRUDDEN (*Arch. exp. Path. Pharm.*, 1910, 62, 374—379).—Experiments on dogs show that after subcutaneous administration of morphine, the fæces contain much more of the alkaloid if at the same time the activity of the intestine is increased by appropriate drugs. W. D. H.

Occurrence of *l*-Hydroxyphenyl-lactic Acid in the Urine of Dogs Suffering from Phosphorus Poisoning. YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, 65, 397—401).—See this vol., i., 384.

Occurrence of *p*-Hydroxymandelic Acid in the Urine in Cases of Acute Yellow Atrophy of the Liver. ALEXANDER ELLINGER and YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, 65, 402—413).—See this vol., i., 384.

The Different Action of Barium Chloride on the Frog's Heart when Applied Internally and Externally. E. POULSSON (*Arch. exp. Path. Pharm.*, 1910, **62**, 365—373).—Internal application of barium chloride to the isolated frog's heart produces systolic stoppage, whilst if it is applied externally, the result is diastolic pauses. This is analogous to, but not so regular and constant as, what has been previously described for substances of the digitalis group.

W. D. H.

Mixed Narcosis and Combined Narcosis. W. MADELUNG (*Arch. exp. Path. Pharm.*, 1910, **62**, 409—428).—The total effect of two indifferent narcotics, such as ether and chloroform, is not the arithmetical sum of the two actions. If non-narcotic doses of morphine-scopolamine are given, deep narcosis can be induced with comparatively small amounts of a volatile anæsthetic, and even with laughing gas.

W. D. H.

Narcotics and Local Anæsthetics. OSCAR GROS (*Arch. exp. Path. Pharm.*, 1910, **62**, 380—408).—Local anæsthetics are protoplasmic poisons; their action on muscle is, within certain limits, reversible. Local anæsthetics are probably strong narcotics. Narcotics inhibit the irritability of motor nerves in certain concentrations, and this action is usually reversible; these concentrations are about six times greater than those which Overton gives for their narcotic action, that is, the central nervous system is about six times more sensitive than the peripheral; sensory nerves are in this relationship on the same level as motor nerves. W. D. H.

Action of an Active Principle from Apocyneum. H. R. DALE and PATRICK P. LAIDLAW (*Heart*, 1909, **1**, 138—165).—Crystalline apocynin (acetovanillone) has but the feeblest physiological action when pure. The true active principle is a crystalline, non-glucosidal substance, to which the names *cynotoxin* and *apocynamarin* have been given by previous workers. Its action in all respects resembles that of the digitalis series, but it is apparently not cumulative.

W. D. H.

Experimental and Clinical Observations on Disturbances of Sympathetic Innervation (Adrenaline-mydriasis) and on Intestinal Glycosuria. EMIL ZAK (*Pflüger's Archiv*, 1910, **132**, 147—174).—Adrenaline produces its effects by acting on sympathetic nerve-endings, and among other effects is that of pupillary dilatation. Loewi showed that after extirpation of the pancreas, adrenaline no longer causes mydriasis. In frogs, dogs, and rabbits, it was shown that corrosion of the intestinal tract by alkali causes transitory glycosuria, and also Loewi's pupil phenomenon; this is also transitory; corrosion of the large intestine, however, produces neither effect. The effects are slight in rabbits. In the present research, it is shown that the two phenomena are not so intimately associated as Loewi supposed, and that adrenaline mydriasis cannot be the simple result of sympathetic stimulation; clinical observations on man are recorded which confirm this view. W. D. H.

The Action of Pure Choline on Blood-Pressure. EMIL ABDERHALDEN and FRANZ MULLER (*Zeitsch. physiol. Chem.*, 1910, **65**, 420—430).—Mott and Halliburton (Abstr., 1899, ii, 315, 781) stated that choline produces a fall of arterial blood pressure unless atropine has been given previously, when it produces a rise. Modrakowski (Abstr., 1908, ii, 974) stated that pure choline always raises the pressure. In the present paper the original statements of Mott and Halliburton are confirmed. The typical action of choline is a depressor one; any pressor effect is due to accidental circumstances. Certain points in relation to the antagonism of choline and adrenaline (on blood-pressure, uterus, iris, etc.) are also referred to.

W. D. H.

Estimation of the [Physiological] Activity of Certain Members of the Digitalin Group. ROBERT KRAILSHEIMER (*Arch. exp. Path. Pharm.*, 1910, **62**, 296—304).—The relative activities of these substances were estimated by the time in which they produced stoppage of the frog's heart. Digitoxin, strophanthin, and antiarin are about equal. Oleandrin and erythrophlein are less toxic, and digitalein and digitalin least so. Four milligrams of digitalein correspond with three of digitalin and 0·1 of digitoxin. W. D. H.

The Behaviour of Phloridzin after Extirpation of the Kidneys. ERICH LESCHKE (*Pflüger's Archiv*, 1910, **132**, 319—337).—After intravenous injection of 1 gram of phloridzin in nephrectomised rabbits, it can be detected subsequently in the blood. After subcutaneous injection in similar animals, absorption of the drug is so slow that hours afterwards phloridzin can be found at the seat of injection. That which is absorbed is so greatly diluted that large amounts of blood or organ extracts must be employed to detect it. These results are at variance with those of Glaessner and Pick. Phloridzin is very toxic to rabbits; under 1 gram is often fatal from cardiac failure; there are also poisonous effects on the central nervous system (contraction of pupil, convulsions, cessation, following an exaggeration, of the breathing). W. D. H.

The Mechanism of the Depressor Action of Dog's Urine, with some Observations on the Antagonistic Action of Adrenaline. RICHARD M. PEARCE and ARTHUR B. EISENBREY (*Amer. J. Physiol.*, 1910, **26**, 26—31).—Intravenous injection of dog's urine causes an abrupt but transient lowering of arterial pressure. This is antagonised by adrenaline and by barium. Possibly the depressor substance, previous to elimination, plays a part in regulating the action of adrenaline. If nerve-endings are paralysed by *apo*codeine, neither urine or adrenaline produces their effects; both substances act on the sympathetic nerve-endings.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Koch's Bacilli. Medium Containing Glycerophosphates. Maximum Proportion of Iron and Manganese. G. BAUDRAN (*Compt. rend.*, 1910, **150**, 1200—1202).—Analysis of the ash of tubercle bacilli and of the bouillon in which they are cultivated led to the preparation of a liquid having the following composition, and which has been found to give excellent results as a culture medium: sodium citrate 4 grams, glycerol 50 grams, Byla's albumose 10 grams, the following glycerophosphates, sodium 2·24 grams, potassium 0·6 gram, calcium 1·2 grams, magnesium 1·76 grams, water 1 litre. The solution is sterilised at 100°.

The maximum proportion of manganese admissible is 3 grams, of iron 3·10 grams, both being present as glycerophosphates. The latter corresponds with the amount of iron in 1 litre of blood.

W. O. W.

Fermentation of Tyrosine. F. TRAETTA-MOSCA (*Gazzetta*, 1910, **40**, i, 86—102).—The author has isolated from horse-dung a bacillus which is able to grow in a nutritive liquid containing only mineral salts and tyrosine, and to decompose the latter, giving, first, hydro-*p*-coumaric acid, and later, benzoic acid and benzene. The decomposition is apparently a gradual one, consisting successively of de-amidation, oxidation, reduction, and de-carboxylation. Estimation of the carbon dioxide developed during the fermentation of the tyrosine shows that decomposition of the latter proceeds until the nucleus is completely destroyed, the final products doubtless consisting of carbon dioxide, water, and ammonia. The organism also grows well in a solution containing, as sole organic constituent, hydro-*p*-coumaric, *p*-hydroxybenzoic, or benzoic acid, but does not develop in a liquid containing only mineral acids and *o*- or *m*-hydroxybenzoic acid. The cultural and morphological characters of the bacillus are described.

T. H. P.

Biology and Chemistry of Nitroso-Bacteria. GEORGE E. GAGE (*Centr. Bakt. Par.*, 1910, ii, **27**, 7—48).—The weakest strains of *Pseudomonas radicicola* can be made capable of fixing considerable amounts of nitrogen by constantly growing on non-nitrogenous media. As regards the utilisation of sugar, it was found that maltose gives the best results; with carbohydrates containing less than five carbon atoms, gum is not produced.

In old cultures, especially on solid media, *Pseudomonas radicicola* develops a membrane which appears cell-like in structure, but does not give cellulose and starch reactions. When inoculated from such cultures into artificial culture solutions it may be capable of producing considerable amounts of nitrites and nitrates. There is, at present, no evidence that nitrates are produced without nitrite production.

N. H. J. M.

Soil Bacteriology. ADAM DZIERZBICKI (*Bull. Acad. Sci. Cracow*, 1910, *B*, 21—66).—The author emphasises the necessity for making a chemical study of the soil simultaneously with bacteriological investigations. Remy's method only gives useful and consistent results when the chemical composition of the solution is such that it is practically unaffected by the addition of the soil used for inoculation. Nitrogen fixation is considerably influenced by the amount of available mineral matter present; any lack of available calcium and potassium compounds and of phosphates is distinctly unfavourable. Humus is also desirable; hence in making up a culture solution for investigating nitrogen fixation some sodium humate should be added, as well as the usual mannitol and mineral substances. Potassium phosphate is better than a mixture of monocalcium phosphate and potassium chloride.

E. J. R.

Relation of Methylpentosans to Pentosans in Some Kinds of Seeds. GUIDO BORGHESANI (*J. Landw.*, 1910, **58**, 77—79).—The amounts of methylpentosans and pentosans were estimated in (1) five varieties of Soja beans, and (2) four varieties of maize. The average amounts were as follows: Methylpentosans (1) 0·48; (2) 0·46%. Pentosans (1) 2·98; (2) 2·47%.

N. H. J. M.

A Peculiar Type of Plant Respiration. S. KOSTYTSCHEW (*Zeitsch. physiol. Chem.*, 1910, **65**, 350—382).—As a rule, fermentable carbohydrates alone are broken down during respiration; even where fats serve as the respiratory material they are probably first converted into sugar. In absence of air, the sugars do not oxidise, but are converted into carbon dioxide and alcohol, which may be regarded as the general products of anaerobic respiration.

The author finds that a mushroom, *Psalliota compestris*, shows exceptional behaviour, as probably do other Hymenomycetes containing no soluble carbohydrates. No alcohol is formed, but carbon dioxide is evolved. Müntz's observation that hydrogen and alcohol are both formed was not confirmed. A number of experiments were made with the pressed juice of the mushroom, indicating that oxygen is readily absorbed, and also that carbon dioxide is readily evolved; the latter process is not enzymic, since it is not inhibited by boiling the solution or by addition of lime-water, which precipitates the proteins. The author applies Bach and Engler's autoxidation hypotheses, and considers that they explain the facts.

E. J. R.

Action of Useful and Injurious Stimulants on the Respiration of Plants. N. N. IVANOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1910, [vi], 571—581. Compare this vol., ii, 438; Palladin, this vol., ii, 438).—The results of experiments on etiolated bean twigs and wheat embryos show that the actions of poisons on the respiration of living and dead plants may be divided into three classes: (1) The living plants are stimulated and the dead ones oppressed, or else the two behave similarly; (2) the living objects are not at all or but slightly oppressed, the dead ones being oppressed to a considerably greater extent; (3) both the living and dead plants

are either equally oppressed or else indifferent. The respiration was measured by means of the volume of carbon dioxide evolved.

T. H. P.

Osmotic Pressure in Plants. Thermo-electric Method of Determining Freezing Points. HENRY H. DIXON and W. R. GELSTON ATKINS (*Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 275—311).—Osmotic pressures vary with the species and individual. Leaves of the same individual, under similar conditions, have the same osmotic pressure, whilst under varying conditions considerable variations are found, due probably to fluctuations in the carbohydrate-contents of the cells. Assimilation results in a rise in the osmotic pressure and in the mean mol. wt. of the solutes. Similar results, but less marked, are seen when detached leaves are stored in the dark. These changes are attributed largely to the hydrolysis of sucrose and starch.

The osmotic pressure of leaves attached to a plant may be considerably reduced by shielding from light.

The greatest depression of freezing point was shown by the sap of *Syringa vulgaris* ($-2\cdot234°$, corresponding with an osmotic pressure of 26·87 atmospheres); the smallest depression was in the sap of *Chamaerops humilis* ($-0\cdot315°$, equivalent to an osmotic pressure of 3·79 atmospheres).

In summer, when the leaf cells of *Syringa* contain greater amounts of sugars, pressures from 30 to 40 atmospheres are not improbable.

N. H. J. M.

Position at which the Nitrogen of Nitrates is Utilised in Plants. CAMILLO ACQUA (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 339—344).—When ordinary wheat is treated with a solution of a radioactive salt, such as uranyl nitrate, examination of the corns by the electroscopic method reveals an accumulation of active material in the root-apices, whilst microscopic examination of the tissues shows the formation of an insoluble, yellow deposit of uranic oxide (?): firstly in the dermatogen near to the apex, and, on prolonged culture, in the adjacent lower layers of tissue. As this deposit is formed by uranyl nitrate and scarcely at all by other uranium salts, the author regards the phenomenon as due to the decomposition of the nitrate with utilisation of the nitrogen by the plant, and consequent deposition of the oxide. Uranium having an injurious action on plants, the author has carried out preliminary experiments on the action of manganous nitrate solutions on wheat and the ordinary bean. The results are similar to those given by the uranyl salt, an insoluble, black deposit being formed. With manganous chloride and sulphate, no deposits were obtained.

T. H. P.

Absorption of Barium by Plants. H. COLIN and J. DE RUFZ (*Compt. rend.*, 1910, **150**, 1074—1076).—Experiments on the cultivation of peas in dilute solutions of barium nitrate and chloride (0·0125%) indicate that the plants, especially the roots, are capable of absorbing appreciable amounts of barium. The metal appears to be

localised, and its distribution to correspond with certain granulations in the pericycle. W. O. W.

Variation in the Amount of Sparteine in Common Broom. JACQUES CHEVALIER (*Compt. rend.*, 1910, **150**, 1068—1069).—Sparteine is produced more rapidly during the early life of the plant than during the flowering season, or after this period. The seeds at maturity contain 1·1% of the alkaloid. W. O. W.

Constituents of Cauliflower. ROMAN DMOCHOWSKI and BERNHARD TOLLENS (*J. Landw.*, 1910, **58**, 27—31).—The composition of (1) the flower, and (2) the stalk, was found to be as follows:

	Water.	Crude protein.	Crude fat.	Cellulose.	Pentosan.	Methyl-pentosan.	N-free extract.*	Crude ash.
1.	90 84	2·95	0·25	1·05	0·87	0·26	2 78	1 00
2.	90·84	2·11	0·15	1·50	1·15	0·27	2·81	1·17

* Excluding pentosan and methylpentosan.

Dextrose and lævulose were found to be present, but not sucrose. N. H. J. M.

The Fruit of Cornacea stolonifera. JAY DUNCAN (*Chem. News*, 1910, **101**, 217—218).—The dry berries contain 3% of ash, 11·5% of a substance resembling dextrin, about 38% of sugars, and 3·5% of fixed oil. The sugars present include dextrose and maltose. Tartaric, oxalic, or citric acid could not be detected. T. A. H.

Presence of Betaine in the Tubers of Helianthus tuberosus. ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1910, **65**, 293—294).—By means of the method of separation described in a former paper (Abstr., 1909, ii, 605), the author has shown the presence of betaine in the tubers of this plant. From 25 kilos. of the tubers, 2 grams of betaine hydrochloride could be obtained. The substance was identified by means of a number of derivatives. R. V. S.

Presence of Hydrocyanic Acid in the Order Thalictrum. LEOPOLD VAN ITALLIE (*Pharm. Weekblad*, 1910, **47**, 442—448; *Arch. Pharm.*, 1910, **248**, 251—256. Compare Abstr., 1905, ii, 852).—An investigation of the amount of hydrocyanic acid present in plants of the *Thalictrum* order at various periods of the year. The seeds of *Thalictrum aquilegifolium* and *T. angustifolium* alone contain hydrocyanic acid. A. J. W.

Mineralogical Significance of Vegetation Experiments. J. SAMOILOFF (*Centr. Min*, 1910, 257—262).—Powdered minerals in a fresh, unweathered condition were added to soils or other media which had been deprived of certain elements necessary for the growth of plants. As shown by the rates of growth in such experiments, it is evident that inorganic nourishment can be extracted more easily from some minerals than from others. It is therefore suggested that this method of investigation, like that given by the study of weather-

ing products, may throw some light on the chemical constitution of minerals, and especially in the case of dimorphous minerals, such as calcite and aragonite, and orthoclase and microcline.

Wheat, vetch, etc., were grown in quartz-sand together with (1) orthoclase (from St. Gottard and from Mursinka), and (2) microcline, with practically the same results for both minerals, although a more profuse growth was obtained with sanidine, Apophyllite and leucite produced about the same result as orthoclase, but phillipsite gave a greater profusion of growth, indicating that potassium can be more easily extracted from this zeolitic mineral.

Of lower organisms, cultures of *Aspergillus niger* were found to thrive better on mica (muscovite and biotite) than on felspar (orthoclase and microcline). L. J. S.

Function of Micas in Arable Soils. BIÉLER-CHATELAN (*Compt. rend.*, 1910, 150, 1132—1135).—Experiments on pot culture with artificial soils have shown that the roots of some plants are capable of assimilating the potassium of insoluble silicates, such as white mica, and consequently the presence of these minerals in soils is not without advantage. The suggestion is put forward that mica, with apatite and tourmaline, may be the principal source of the fluorine found in plants. W. O. W.

Nature of the Colour of Black Cotton Soils [in India]. H. E. ANNETT (*Mem. Dept. Agric. India*, 1910, 1, 185—203).—The dark colour of the black cotton soil of India, which covers an area of quite 200,000 square miles, was generally supposed to be due to organic matter. It was shown by Leather, however, that the soil does not contain high amounts of organic matter, and that when this is destroyed by sulphuric acid the residue was still black; and the conclusion was drawn that the dark colour is due to the presence of a black mineral. This view is now shown to be substantially correct, although the colour is in part attributed to organic matter.

The black mineral, which is magnetic, forms lustrous crystals, D about 5·7. A sample, freed as far as possible from earthy matter, was found to contain: MgO, 3·32; Fe_2O_3, 73·24, and TiO_2, 18·07. N. H. J. M.

Nitrogen Economy of Arable Soils. THEODOR PFEIFFER, AUGUST GUTTMANN, and F. THIEL (*Mitt. landw. Inst. kgl. Univ. Breslau*, 1910, 5, 657—713).—Numerous pot experiments were made to ascertain the amounts of nitrogen fixed by soil, in its natural state, after fallow, oats, and mustard respectively; in the same soil sterilised by heating in steam under 3 atmospheres pressure; in the soil treated with carbon disulphide, and in soil to which sugar was added. The experiments were made in pots holding 13 kilos. of loam. The amounts of produce obtained in the different series, and the nitrogen in crops and soil were determined.

The results invariably showed gains of nitrogen from 0·778 to 1·275 grams, the average gain being 1·034 grams per 13 kilos. of soil (compare Joulie, *Ann. Agron.*, 1886, 12, 5, and Berthelot, Abstr., 1887, 395). The greatest gain after fallow was in the soil treated with

carbon disulphide (1·275 grams), then in the steamed soil (1·031 grams), and in the natural soil the gain was 0·901 gram. The nitrogen in the produce was highest in the steamed soil; carbon disulphide had very little effect, whilst addition of sugar reduced the amount of nitrogen taken up by the plants, although the soil showed a distinct gain. The total gain (in soil and crop) was practically the same with sugar as without it. The soil in its natural condition (without carbon disulphide or sugar) showed gains of nitrogen in addition to the nitrogen of the crops.

Sand culture experiments with soil algæ showed that with luxuriant growth the gain of nitrogen was only slight. N. H. J. M.

Fixation of Nitrogen in the Soil with the Help of Cellulose as Source of Energy. ALFRED KOCH (*Centr. Bakt. Par.*, 1910, ii, 27, 1—7. Compare Pringsheim, this vol., ii, 230).—Soil to which paper (0·33%) was added was found to be quite free from nitrates about nine months later. Subsequently, after the paper had disappeared, nitrates were again found to be present. Experiments with buckwheat and mangolds grown in soil mixed with sand, both without and with paper, showed enormous reductions in the amount of produce when paper was present, due, no doubt, in part to the destruction of nitrates.

Further experiments are described in which liquid cultures containing paper (12 grams) were inoculated from soil, from vegetable refuse, and from dung, and then covered with soil. After six months, it was found that with soil bacteria alone only 1·2 grams of cellulose was destroyed; with bacteria from vegetable matter and from dung, the amounts of cellulose destroyed were 3·85 and 10·35 grams respectively. The amounts of nitrogen fixed, coincident with the destruction of cellulose, were 9·04, 13·68, and 102·2 mg.

The divergent results obtained with cellulose would thus seem to be due to different cellulose organisms. The beneficial action of farmyard manure is probably largely due to the introduction of cellulose bacteria favourable to nitrogen-fixing organisms; and the increased effect of green manure by the addition of farmyard manure is to be attributed to the action of organisms introduced with the latter on the cellulose of the green manure, rather than to any increased decomposition of nitrogenous matters. N. H. J. M.

Denitrification and Accumulation of Nitrogen in Soils. FRANCIS S. MARR (*Mitt. landw. Inst. kgl. Univ. Breslau*, 1910, 5, 639—656).—Experiments are described in which a loam soil (3 kilos. per pot) to which straw (0·5%) and sucrose (2 and 8%) respectively were added, in some cases with further addition of sodium nitrate (0·15%), was kept for about three months at 30°, the total nitrogen being determined at the commencement, after six weeks, and at the conclusion. Pots containing soil only were included in the experiment, and some of those containing straw (or sucrose) and nitrate were aerated every two or three days.

The soil alone (which contained 0·133% N) showed a slight gain of nitrogen in the first period, followed by a slightly greater loss in the

second. Addition of straw resulted in a decided gain (0·173 gram) in the first, and a loss (0·094 gram) in the second, period, whilst with 2% of sucrose there was a gain of 0·079 gram in the first period and a gain of 0·053 gram in the second. With the soil containing 8% of sucrose, in which only the initial and final amounts of nitrogen were determined, there was a gain of 0·150 gram N.

When sodium nitrate was supplied in addition to straw, the gain of nitrogen in the first period was reduced from 0·173 to 0·008 gram, whilst the loss in the second period was increased. Similar results were obtained with 2% of sucrose + nitrate in the first few weeks; in the second period there was still a gain, but greatly reduced as compared with sucrose alone. Where nitrate was added to the soil containing 8% of sucrose, there was a slight loss (0·005 gram) instead of the gain of 0·150 gram.

Aeration of the soil containing organic matter + nitrate considerably reduced the final loss in the case of straw, and had no appreciable effect on the final result with 2% of sucrose. With 8% of sucrose and nitrate the loss was increased to 0·203 gram. N. H. J. M.

The Retention of Superphosphate in Soils. IGNAZ K. GREISENEGGER (*Zeitsch. landw. Vers.-wesen. Oesterr.*, 1910, **13**, 1—47).—A comprehensive study of the mode of occurrence, the distribution, and retention of phosphorus in soil and plants. Three types of soil were studied: (1) a rich alluvial loam, (2) a light sandy loam, (3) a strong soil, rich in humus and manurial deposits; these were submitted to mechanical and chemical analysis, and plants grown in them likewise examined at different stages of growth, the phosphorus content in the different organs being separately estimated. Numerous pages of tabulated results are appended. F. M. G. M.

Calcium Cyanamide and Some of its Decomposition Products. ALBERT STUTZER and F. REIS (*J. Landw.*, 1910, **58**, 65—76).—Calcium cyanamide remains unchanged for a long time in the soil, and acts injuriously on germination. It is, however, without injurious action when applied to growing plants when the soil contains other available forms of nitrogen. Production of dicyanodiamide from calcium dicyanamide in the soil need not be feared. The latter is not injurious to bacteria, yeast, and *Streptothrix* when other sources of nitrogen are present.

The first process in the decomposition of calcium cyanamide is the absorption of carbon dioxide. This is followed by the decomposition of the cyanamide, mainly chemical and not biological, into urea and similar compounds. The most important soil constituent concerned in this change is ferric oxide. The urea is rapidly converted into ammonia, and subsequently into nitrates. Dicyanodiamide is not available as a source of nitrogen for higher plants.

Dicyanodiamidine and diguanidine sulphate are utilised by *Penicillium glaucum* and *Aspergillus oryzae*. Soil and water bacteria are very sensitive, and both compounds are injurious to the germination of seeds. N. H. J. M.

The Efficiency of Calcium Cyanamide, Chili Saltpetre, and Ammonium Sulphate. JOHANN J. VAŇHA (*Zeitsch. landw. Vers.-wesen.*, 1909, **12**, 785—838).—A detailed account of numerous experiments in which varying quantities of calcium cyanamide, Chili saltpetre, and ammonium sulphate were applied to various soils under different crops, either alone or in conjunction with phosphatic, lime, and other manures. Numerous tabulated results, with discussions on their significance, are given in the paper. F. M. G. M.

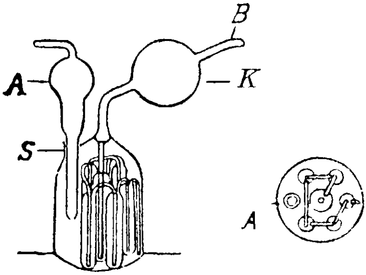
Manurial Experiments on Peat Soil with "Pàlmaer Phosphate," a New Manure Prepared by an Electrolytic Process. HJALMAR VON FEILITZEN (*J. Landw.*, 1910, **58**, 33—43).—The manure is produced by the following process. A solution of sodium chlorate or perchlorate is electrolysed, and the acid anode liquid allowed to act on crude phosphate, which it dissolves. The saturated solution is then treated with the alkaline cathode liquid until only slightly acid, when dicalcium phosphate separates as a fine, crystalline powder; the yield is almost quantitative. The calcium in solution is precipitated in part as hydroxide by adding the rest of the alkaline solution, and the remainder as carbonate by passing in carbon dioxide (Soderbaum, *Zeitsch. landw. Vers.-wesen. Oesterr.*, 1908, 506). The manure contains 36—38% of phosphoric acid, of which about 95% is citrate-soluble.

The results of pot and field experiments on peat soil with oats, peas, lupins, and potatoes showed that the manure is equal in value to superphosphate and basic slag. N. H. J. M

Analytical Chemistry.

[Absorption and Extraction Apparatus. Weighing Pipettes.] ERNST BERL (*Chem. Zeit.*, 1910, **34**, 428—429).—*Absorption Apparatus*, Fig. 1.—The ground joint *S*, which is slightly greased, serves for the introduction by means of a pipette of the absorbent, and is fitted with the vertical bulb-tube *A*, which is plugged with glass wool and filled with granulated calcium chloride. On applying suction at *B*, the solution ascends into *K*; by blowing, it fills the six separate absorption cells. When filled with aqueous potassium hydroxide (1 : 1), the apparatus weighs about 60 grams.

FIG. 1.



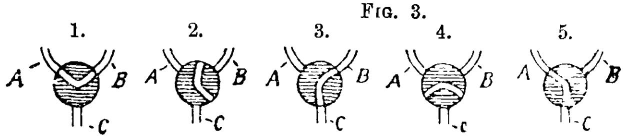
Weighing Pipette, Fig. 2.—An improvement on the Lunge-Rey

pipette, being much less in weight, although the bulb is larger. When required for use, the three-way cock, Fig. 3, is placed as figured in (1), and suction is applied at A, causing a diminished pressure in K. The stopcock is now turned as figured in (2); the point of the pipette is immersed in the liquid, and, after turning the stopcock as figured in (3), the liquid is drawn by suction into the pipette and the stopcock turned as figured in (4).

The stopper of the bulb K is momentarily lifted, the point S is wiped dry, and the pipette placed in its support. After weighing, the stopcock is turned as figured in (5); the apparatus is emptied partly or completely, and then reweighed after turning the stopcock in position (4).

Modified Weighing Pipette, Figs. 4 and 5.—In weighing liquids of

FIG. 3.



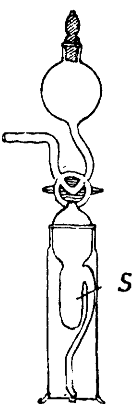


FIG. 4.

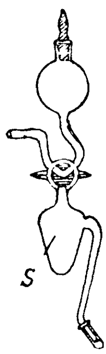


FIG. 5.

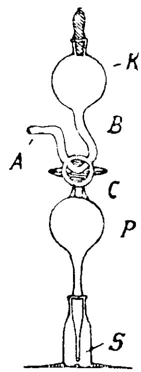


FIG. 2.

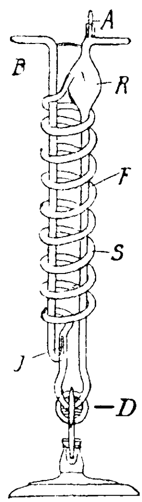


FIG. 6.

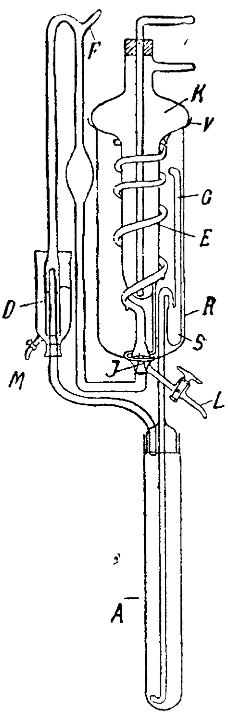
considerable vapour-tension in a pipette, the liquid is apt to drop during the weighing; to prevent this, the modified form has been devised in which, on suction, the liquid enter the bulb S. When emptying the pipette, the pipette is inclined, and the stopcock turned in position (5). The pipette may be weighed either by placing it in a support, or it may be suspended from the balance.

Modified Winkler Serpentine Tube, Fig. 6.—The absorption liquid is introduced into A by means of a pipette. The liquid expelled by the gas entering through B enters the reservoir R, runs from there into the tube F, to be again forced upwards through the spirals by the gas injected at the point T. When first passing the gas, the the three-way cock D is turned as figured in (2) (Fig. 3); the gas ascends from the injection point T into the worm S. When this is filled with gas bubbles, the stopcock is turned as in (1) (Fig. 3).

The tube *F* is now in direct communication with the injection point, and the liquid collecting in *R* again descends through *F*, and so keeps on circulating. The absorption liquid may be drained after turning the stopcock as figured in (3 and 5) (Fig. 3).

Extraction Apparatus, Fig. 7.—*A* is a boiling tube connected by means of a ground joint with a reservoir *R*, holding about 500 c.c. and containing the liquid to be extracted. In this reservoir is placed the removable glass worm arrangement *E*, furnished with a cooler *K*, also removable. Near this is placed the overflow tube *G* for the solvent; a part of this tube may, if necessary, be disconnected. By way of precaution, a bulb has been introduced at *S* so as to retain any heavy liquid accidentally passed over.

FIG. 7.



When required, 30 c.c. of the solvent and some very small stones are placed in *A*, and the reservoir *R* is placed on. At *D*, mercury is poured into about two-thirds of the content of the beaker; the object of the mercury seal being to avoid too strong a tension in the apparatus, and also to serve as a safety valve in case of a stoppage in the injection point *T*. The liquid to be extracted is now placed in *R* up to about 3 cm. below the end of the tube *G*, the glass worm is put in, the solvent is added, and the cooler is fixed in. After making a water seal between the cooler and *R*, heat is applied to *A*, and a current of air or other inert gas is passed through the inlet tube *F*. This, mixed with the vapours of the solvent, enters through *T*, below the spirals *E* of the reservoir *R*. The vapour of the solvent condenses in the cooled liquid in very fine drops, which, together with the neutral gas and the attracted liquid, rise through the worm-tube and are ejected at its open end. The two layers soon separate, and the solvent accumulating on the surface runs continually through *G* back into *A*. Owing to the mechanical action of the current of air, the extraction is soon completed.

When the operation is finished, the liquid is drawn off by turning stopcock *L*, and the remainder of the solvent is then collected. The mercury is drawn off by turning stopcock *M*, and the apparatus is then disconnected and cleaned. L. DE K.

Decanting Apparatus for Laboratory Purposes. M. NETTO (*Zeitsch. angew. Chem.*, 1910, **23**, 784).—A swing apparatus in which a basin or beaker can be securely held. By means of a long screw working in a nut, the apparatus can be gradually turned on its axis, and the liquid decanted off without fear of disturbing the precipitate. L. DE K

Cleaning of Platinum Wires for Flame Coloration Experiments. Lucien L. de Koninck (*Bull. Soc. chim. Belg.*, 1910, **24**, 197—198).—For the removal of traces of copper, barium, and other compounds from platinum wires, the author recommends the use of a borax bead, which is allowed to flow two or three times over the contaminated portions of the wire. H. M. D.

Use of Phosphorus Solutions in Gas Analysis. Mieczyslaw Centnerszwer (*Chem. Zeit.*, 1910, **34**, 494—495).—Instead of absorbing oxygen from gaseous mixtures with solid phosphorus, which in presence of very much oxygen is somewhat inactive, the author recommends using a solution made as follows: 230 c.c. of castor oil are placed in a 250 c.c. flask, and 3 grams of dried phosphorus are added. The flask is then stoppered and heated in an oil-bath to 200°, when it is thoroughly shaken until the phosphorus is completely dissolved. The solution is used in the same way as the other gas-absorbents, and the absorption of oxygen is complete when no more luminosity is noticed. When dealing with highly oxygenated mixtures, the oxidation of the phosphorus must be accelerated by warming; for this purpose an electric arrangement is described and illustrated in the original article. L. de K.

Estimation of the Intensity of Acidity and Alkalinity with 2:5-Dinitroquinol. Lawrence J. Henderson and Alexander Forbes (*J. Amer. Chem. Soc.*, 1910, **32**, 687—689).—It is pointed out that although there are many indicators capable of sharply marking the end-point in a titration, there has not hitherto been any indicator suggested which is suitable for measuring all intensities of hydrogen ion concentration.

It has now been found that 2:5-dinitroquinol is well adapted for this purpose. This substance dissolves in water to form a bright orange-coloured solution, which is turned pale greenish-yellow by moderately strong acid, and deep purple by moderately strong alkali. Between these extremes there is a wide range of colours which renders it possible to estimate the concentration of hydrogen and hydroxyl ions in a solution with considerable rapidity and accuracy. Eleven different intensities of reaction can be distinguished, all that is necessary being to prepare a series of standard solutions, and then to compare the colour produced in the solution under examination with the standards. E. G.

A Method of Titrating Physiological Fluids. George S. Walpole (*Proc. physiol. Soc.*, 1910, xxvii—xxix; *J. Physiol.*, **40**).—The difficulty of titrating coloured physiological fluids may be obviated by taking four glass cells, A, B, C and D; A is placed over C, and B over D, and these are illuminated from below, the observer looking down through them. A contains x c.c. of the sample to be titrated; B contains the same + y c.c. of the indicator; C contains y c.c. of the indicator + x c.c. of Sörensen's mixture; D contains water. Standard acid or alkali is added to B until the colour seen on looking down BD is the same as that seen on looking down AC. When the colours match, the contents of B have the same ionic concentration as the

chosen Sörensen mixture. By modifying the arrangement of the tubes so that they are placed $\begin{smallmatrix} C & D \\ A & B \end{smallmatrix}$, the ionic concentration of a feebly acid or alkaline mixture can be measured. The Sörensen mixture in C is altered until a match is obtained. The ionic concentration of the solution in B is then the same as in C, and can be discovered from Sörensen's tables. W. D. H.

Gravimetric Estimation of Free Bromine and Chlorine, Combined Iodine, and Oxidising Reagents by means of Metallic Silver. CLAUDE C. PERKINS (*Amer. J. Sci.*, 1910, [iv], **29**, 338—340. Compare Abstr., 1909, ii, 932).—A definite volume of the aqueous solution of free bromine or chlorine is added to a solution of potassium iodide, acidified with hydrochloric acid, and the solution now containing free iodine is shaken with a sufficiency of electrolytically deposited silver in an atmosphere of hydrogen. The increase in weight of the silver equals iodine, which is then calculated to either bromine or chlorine.

Potassium iodide may be analysed by adding a sufficiency of potassium nitrite or hydrogen peroxide. On acidifying with hydrochloric acid, the iodine is liberated, and may then be removed by shaking with a known weight of silver.

The process may be also applied successfully to the assay of oxidising agents, such as potassium permanganate, hydrogen peroxide, potassium dichromate, and ferric chloride. An excess of potassium iodide is added, and then some hydrochloric acid, and the iodine liberated is removed by silver as directed previously. L. DE K.

Reaction between Hydriodic Acid and Bromic Acid in the Presence of a Large Amount of Hydrochloric Acid. D. L. RANDALL (*J. Amer. Chem. Soc.*, 1910, **32**, 644—646).—Andrews (Abstr., 1903, ii, 686) has shown that when a solution of potassium iodide containing a considerable quantity of hydrochloric acid is titrated with standard potassium iodate, the following reaction takes place:

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O.$$

It has now been found that potassium bromate can be substituted for the iodate in the estimation of iodides, but that the bromate is a more powerful oxidising agent, since the bromine itself reacts with one atom of iodine. The reaction is represented by the equation:

$$3KI + KBrO_3 + 6HCl = 4KCl + 3H_2O + 2ICl + IBr.$$

E. G.

Estimation of Fluorine in Fluorite by Jannasch's Method. JOSEF LOCZKA (*Zeitsch. anal. Chem.*, 1910, **49**, 329—340).—A slight modification of the platinum apparatus and the process used by Jannasch [and Röttgen] (Abstr., 1895, ii, 460). Illustrations are given of both the original and new apparatus. In the original process the fluorite is heated with sulphuric acid in simultaneous currents of air and carbon dioxide, and the gases passed through aqueous sodium hydroxide, but the author now uses a current of air first, and, after some six hours, a current of carbon dioxide is passed for some two hours.

It is pointed out that when subsequently separating the calcium carbonate from the calcium fluoride, great care should be taken that no excess of acetic acid is used, as on evaporating to dryness the acid acts on the calcium fluoride to a serious extent, and so causes a decided loss.

L. DE K.

Estimation of Sulphur and of Halogens in Organic Substances JULIUS MARCUSSON and H. DÖSCHER (*Chem. Zeit.*, 1910, 34, 417—418).—The process is a modification of the Hempel-Graefe method of estimating sulphur by burning the substance in a large volume of oxygen and oxidising the sulphur dioxide to sulphuric acid by the addition of a solution of sodium peroxide from a dropping-funnel (Abstr., 1904, ii, 514). The method is also applicable to the estimation of halogens if sodium hydroxide is introduced in place of the peroxide. Instead of a platinum cone to hold the wadding and the substance, the authors use a shallow, cylindrical platinum vessel suspended by a platinum wire fused into the well-ground glass stopper of the large bottle. The use of a dropping-funnel is obviated by placing the solution of sodium peroxide or hydroxide in the bottle itself. The ignition of the substance and wadding is effected by lighting a thread, one end of which touches the wadding and the other reaches nearly to the glass stopper. The stopper is held firmly in position while the combustion is proceeding. The sulphate or the halide formed, after reduction of any oxyhalide by Devarda's alloy, is estimated in the usual way.

C. S.

Analysis of Sulphur Used for Agricultural Purposes. EUGÈNE COLLIN (*Ann. Falsif.*, 1910, 3, 132—138).—The detection of ground sulphur in flowers of sulphur is of some importance owing to the difference in the prices of the two substances, although considerable conflict of opinion obtains as to their respective insecticidal properties. A microscopical examination of a sample of sulphur will indicate whether a sample consists solely of one kind of sulphur or not, but comparison specimens of the two varieties should be examined at the same time. In the case of a mixture, the quantities of the two kinds of sulphur present may be approximately ascertained by comparison with mixtures containing known amounts. The solubility of the sample in carbon disulphide is also of some use, as freshly sublimed flowers of sulphur yield about 33% of matter insoluble in this solvent; this amount diminishes as the sample is kept, and may decline to 12%, or even less, but any sample of flowers of sulphur yielding less than 12% of insoluble sulphur probably contains ground sulphur.

W. P. S.

Estimation of Sulphur in Metallic Molybdenum and Tungsten and their Iron Alloys. WOLDEMAR TRAUTMANN (*Zeitsch. anal. Chem.*, 1910, 49, 360—361).—Two grams of the powdered metal are placed in a porcelain boat, and burnt in a 35 cm. long combustion tube in a current of pure oxygen. The tube is drawn out at one end so as to minimise contact with the caoutchouc tubing (which may contain sulphur) used to connect it with the

potash apparatus. The sulphur dioxide or trioxide is absorbed in aqueous potassium hydroxide, bromine is added, and, after adding a slight excess of hydrochloric acid, the sulphuric acid is precipitated as usual. L. DE K.

Comparison of Methods for the Estimation of Sulphur in Coal. SAMUEL W. PARR, W. F. WHEELER, and RUTH BEROLZHEIMER (*J. Ind. Engin. Chem.*, 1909, **1**, 689—692).—A discussion and comparison of various methods for estimating sulphur in coal, the publication of which is due to the appearance of papers by Hollinger containing results identical with those of the author, except with respect to a photometric process. The authors find in opposition to Hollinger that fusion with sodium peroxide is satisfactory, if the reagent is specially prepared and the fusion carried out in a special "calorimetric bomb," a sketch of which is given in the paper; a "sulphur photometer curve" and comparative tables of results are also included. F. M. G. M.

Estimation of Free and Combined Sulphurous Acid in Wines. P. CAZENAVE (*Ann. Falsif.*, 1910, **3**, 154—158).—Having found by actual experiment that iodometric estimations of sulphurous acid in wine are untrustworthy, the author recommends that this acid should be estimated gravimetrically after oxidation with iodine. He finds that all free sulphurous acid may be removed from wine by distilling the latter for five minutes under reduced pressure at a temperature below 50°. The residual or combined sulphurous acid is then estimated, and the difference between this amount and that of the total sulphurous acid present gives the quantity of free sulphurous acid. The total sulphurous acid is best estimated by the difference in the quantity of sulphate before and after oxidation with iodine. It is found that it is not necessary to carry out the distillation of the free sulphurous acid in an atmosphere of carbon dioxide. W. P. S.

Estimation of Sulphuric Acid and of Sulphur in Pyrites. MAURICE HUYBRECHTS (*Bull. Soc. chim. Belg.*, 1910, **24**, 177—197).—The author has examined in detail the factors which influence the accuracy of the gravimetric estimation of sulphuric acid by precipitation as barium sulphate. In particular, the effect of the presence of hydrochloric acid, of excess of barium chloride, and of the presence of ammonium and sodium chlorides has been studied. The observations indicate that the best results are obtained when the solution, from which the sulphate is precipitated, contains from 20 to 30 c.c. of 5*N*-hydrochloric acid and 5 to 10 c.c. of a normal solution of barium chloride per 500 c.c. Precipitation should be effected in boiling solution, and the volume reduced to one half by evaporation. Before filtration, the precipitate should be allowed to remain in contact with the solution for about twenty-four hours. Small quantities of sodium and ammonium chloride have very little influence on the results obtained. In the presence of iron, the method of Gyzander (Abstr., 1906, ii, 391), according to which the iron is reduced to the ferrous condition by the addition of hydroxylamine hydrochloride, is found to

give satisfactory results. The solution should be made nearly neutral by alkali before the reducing agent is added, and this should be used in considerable excess. H. M. D.

Estimation of Sulphuric Acid by the "Benzidine Process," Particularly in the Presence of Chromium. Georg von Knorre (*Chem. Zeit.*, 1910, **34**, 405—407).—In the presence of ferric chloride the iron should be reduced to the ferrous state by means of hydroxylamine hydrochloride. When analysing pyrites, the amount of ferric chloride formed may be neglected.

Estimation of sulphuric acid in the presence of chromic salts.—The solution is boiled with excess of ammonium acetate or formate, and then mixed with the usual benzidine solution. The precipitation of the sulphuric acid takes place somewhat slowly, but is complete in a day.

Estimation of sulphuric acid in the presence of chromic acid.—The solution is acidified with hydrochloric acid, and heated with hydrazine hydrochloride. When reduction is complete, the solution is neutralised with ammonia, boiled with excess of ammonium formate, and treated as before.

Sulphuric acid in the presence of but little chromic acid may also be precipitated by adding a little hydrochloric acid and then excess of benzidine solution to which hydroxylamine hydrochloride has been added. L. de K.

Phenolsulphonic Acid Method for the Estimation of Nitrates in Water. II. Composition of the Yellow Compound. Emil M. Chamot and D. S. Pratt (*J. Amer. Chem. Soc.*, 1910, **32**, 630—637).—In an earlier paper (Abstr., 1909, i, 641) it has been shown that the yellow coloration produced when standard phenolsulphonic acid is employed for estimating nitrates in water is not due to picric acid, but to an alkali nitrophenolsulphonate.

The yellow compound has now been isolated, and found to consist of *tripotassium* 6-*nitrophenol*-2 : 4-*disulphonate*,

$$NO_2{\cdot}C_6H_2(SO_3K)_2{\cdot}OK,1\tfrac{1}{2}H_2O,$$

which forms brilliant, highly refractive, orange-yellow, triclinic prisms. This is the only yellow substance which could be detected in treated water residues containing from less than 1 up to 60 parts per million of nitrogen as nitrate. In water residues containing more than 50 parts per million of nitrogen as nitrates, minute traces of picric acid may be formed in the cold, and can be detected microchemically. If the water residues contain a large quantity of nitrates and are heated with the reagent for a long time, appreciable amounts of picric acid may be produced. E. G.

Estimation of Phosphorus in Bronze, Brass, and Similar Alloys in the Presence of Arsenic. E. Schürmann (*Mitt. K. Materialprufgs-Amt. Gross-Lichterfelde West*, 1909, **27**, 474—476).—The estimation of phosphorus in alloys containing arsenic is frequently incorrect, owing to the co-precipitation of arsenic with ammonium molybdate. A method is described in which the bronze after solution

in concentrated hydrochloric acid is cooled and shaken with zinc-magnesium couple, the filtered solution treated with sulphurous acid, and any arsenic remaining precipitated with hydrogen sulphide; the filtrate is then evaporated to dryness, treated with dilute hydrochloric acid, and the phosphorus estimated with ammonium molybdate in the usual manner. F. M. G. M.

The Estimation of Phosphorus in Meat. PERRY F. TROWBRIDGE (*J. Ind. Engin. Chem.*, 1909, 1, 675).—In the estimation of phosphorus in meat, it was found that when ignition was carried out in a platinum dish in a muffle furnace, loss of that element by volatilisation occurred. The method finally advocated is to bake the meat in a tared crucible at 110—120°, and then gently ignite in an open crucible until the organic matter is destroyed, a process often requiring eight to ten hours for completion. It is very important to obtain an ash from which the phosphorus can be precipitated with ammonium molybdate, and the Neumann method of digesting with equal volumes of nitric and sulphuric acids, or for eight to ten hours with nitric and hydrochloric acids, is considered most surely to accomplish this purpose.

F. M. G. M.

Quantitative Volatilisation of Arsenic from Solutions, Arsenic Chloride being Reduced to Arsenious Chloride by Hydrazine Salts. PAUL JANNASCH and T. SEIDEL (*Ber.*, 1910, 43, 1218—1223).—The substance to be analysed is washed into a special distilling flask with a little water and hydrochloric acid, 80—100 c.c. of hydrochloric acid (D = 1·19) added, together with 1 gram of potassium bromide (or concentrated hydrobromic acid) and 3 grams of hydrazine hydrochloride or sulphate. The distilling flask is connected with a condenser by means of a ground-glass joint, and sealed on to the end of the condenser is a 50 c.c. pipette dipping into a receiver containing water. The contents of the flask are distilled until the volume of the residue is 25—30 c.c., the time necessary being about an hour. All the arsenic is volatilised in this one operation, and the amount present in the receiver may then be determined either gravimetrically or volumetrically.

This method is preferable to distillation in a current of hydrogen chloride (compare Abstr., 1908, ii, 430), which takes two to three hours. It is accurate when the arsenic is in the presence of antimony, copper, mercury, silver, lead, tin, bismuth, gold, cadmium, phosphoric acid, and vanadic acid. These other elements or acids can readily be estimated in the residue after volatilisation of the arsenic. T. S. P.

Application of Potassium Ferricyanide in Alkaline Solution to the Estimation of Arsenic, Antimony, and Tin. HOWARD E. PALMER (*Amer. J. Sci.*, 1910, [iv], 29, 399—403).—*Arsenic.*—The solution should contain not more than 0·2 gram of arsenious acid. Excess of potassium ferricyanide (at least five times the theoretical amount) is added, and then 25 c.c. of 20% potassium hydroxide. After a few minutes, the liquid, which should occupy less than 100 c.c., is mixed with 10 grams of ammonium sulphate and then

with 100 c.c. of magnesium mixture (55 grams of magnesium chloride and 29 grams of ammonium chloride are dissolved in a litre of water and 5 c.c. of ammonia are then added), and when the arsenical precipitate has settled, the liquid is filtered and the precipitate washed with weak ammoniacal water. The filtrate is then mixed with dilute sulphuric acid in somewhat large excess, and the potassium ferrocyanide formed in the reaction, which therefore represents the arsenic, is titrated as usual with standard permanganate. If not enough acid is added, a temporary but troublesome deposit appears.

Antimony.—The process is practically the same as for arsenic. The antimony, however, need not be removed before titrating with permanganate, so that the addition of ammonium sulphate is not necessary.

Tin.—The solution containing not more than 0·2 gram of the metal in the stannous state is mixed with an excess of potassium ferricyanide previously dissolved and mixed with the potassium hydroxide solution. To the clear solution is then added ammonium sulphate, and, after heating at 50° or 60°, the tin is completely precipitated. The liquid is filtered, and the precipitate washed with 10% ammonium sulphate solution. The filtrate is then strongly acidified with sulphuric acid, and the potassium ferrocyanide formed titrated with standard permanganate. L. DE K.

Estimation of Silicon in High Grade Ferrosilicon. BERNHARD NEUMANN (*Zeitsch. angew. Chem.*, 1910, **23**, 690).—The author states that he has used the method recommended by Preuss (this vol., ii, 346) since 1907, and has found it to be useful also for ferrochrome and other iron alloys. The mixture of sodium peroxide and potassium hydroxide does not injure a nickel crucible so much as the former alone. L. DE K.

Lead Peroxide in Organic Combustions. MAX DENNSTEDT and F. HASSLER (*Ber.*, 1910, **43**, 1197—1200).—Weil (this vol., ii, 242) has stated that the use of lead peroxide in organic combustions is attended with errors, due to the retention of carbon dioxide. It is now claimed that this is not the case, and that the use of about 10 grams of lead peroxide is permissible in all cases. Commercial lead peroxide frequently contains organic impurities, but it gives up one-half the total amount of carbon dioxide possible below 250—300°, that is, in the treatment before the combustion, whilst the rest is only given up above 400—450°, that is, at a temperature higher than usually attained. To prepare pure lead peroxide, it is advisable to electrolyse lead nitrate and dry the deposit obtained in a vacuum. E. F. A.

Estimation of Carbon in Iron, Graphite, and Tungsten by Combustion. MAX DENNSTEDT and TH. KLÜNDER (*Chem. Zeit.*, 1910, **34**, 485—486).—Dennstedt's simplified organic combustion process is applied, but instead of a glass combustion tube, one made of quartz is used; no iron trough is used to hold the tube, but this is heated directly by the burners.

The combustion is carried on as usual in a current of oxygen, the

iron, in the shape of powder, filings, or turnings, being placed in a porcelain boat. On no account should the heating be started at the end of the boat opposite the current, as this will cause spirting of the mass. After combustion, the mass is powdered, and once more ignited in oxygen if thought necessary. Tungsten may be burnt in an ordinary combustion tube in a current of air. L. DE K.

Estimation of Potassium as Potassium Platinichloride. PAUL ROHLAND (*Zeitsch. anal. Chem.*, 1910, **49**, 358—360).—When analysing potash salts by the platinic chloride method, any sulphates present must be decomposed by means of barium chloride, a slight excess of which cannot be avoided.

By evaporating with platinum chloride at a temperature not exceeding 80°, and extracting the dry mass with methyl alcohol instead of ethyl alcohol, the admixed barium chloride is completely dissolved and a pure potassium platinichloride results. L. DE K.

Use of Phenol in the Estimation of Alkali Earths. LÉON LINDET and BRASART (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 933—936 *).—A solution of phenol in water dissolves calcium oxide, barium oxide, strontium oxide, and magnesium oxide readily, and its use affords a means of obtaining these oxides in solution for the purpose of titration. Carbonates, phosphates, silicates, or iron and aluminium compounds are not soluble in phenol. The method is particularly suitable for estimating the alkalinity of the milk-of-lime used in sugar works. W. P. S.

Estimation of Organically-combined Calcium in Sugar Refinery Products. D. SIDERSKY (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 936—938).—The method proposed is based on the fact that organic salts of calcium react with sodium carbonate, calcium carbonate a neutral sodium salt being formed, and that, until more sodium carbonate has been added than is sufficient to combine with or decompose the organic salts, the solution remains neutral in reaction. The saccharine liquid under examination is first of all titrated with standardised hydrochloric acid, using phenolphthalein as indicator. To the neutral solution is then added, drop by drop, sodium carbonate solution until the mixture just becomes alkaline in reaction. The sodium carbonate solution used should be equivalent in strength to the hydrochloric acid; in the absence of organic salts, the volume of sodium carbonate solution required will be equal to that of the hydrochloric acid used, but if organic salts of calcium are present, the quantity of sodium carbonate needed will exceed that of the acid in proportion to the amount of organic salts. In other words, the excess quantity of sodium carbonate solution is a measure of the organic salts of calcium. This applies when the alkalinity of the liquid is due solely to calcium salts, but it sometimes happens that the alkalinity is partly due to potassium salts, and, in this case, the volume of sodium carbonate solution required will be less than that of the hydrochloric acid used for neutralising the liquid, the difference indicating the alkalinity due to potassium salts. W. P. S.

* and *Bull. Soc. chim.*, 1910, [iv], **7**, 434—439

Detection of Metalloids and Metals in Quantity in Mineral Waters. F. Garrigou (*Compt. rend.*, 1910, **150**, 1002—1003).—The residue from 1 litre of the water is treated with *aqua regia* and several times with hydrochloric acid, evaporating to dryness each time. The chlorides are dissolved, and a little hydrogen sulphide solution is added. A darkening of the liquid or a black precipitate shows that heavy metals or metalloids are present. The filtrate is treated with ammonium sulphide to detect metals of group 3.

The dried precipitates are further examined by flame tests, borax bead, microcosmic salt, reduction on carbon filament or the spectroscope. The method here described is a useful preliminary to a complete analysis, which may require 100 litres of water.

R. J. C.

Detection of Copper and Cobalt by means of Naphtenic Acid. K. W. Charitschkoff (*Chem. Zeit.*, 1910, **34**, 479—480).—The author has proposed some time ago a solution of naphtenic acid in benzene as a delicate test for copper, and now states that it is also useful for the detection of cobalt. When shaken with the reagent, this becomes eosin-red, whilst nickel gives only a pale green, and does not interfere with the test for cobalt. L. de K.

A Process for the Analysis of Bronze, Brass, and other Alloys, and the Electrolytic Estimation of Tin in the Same. E. Schürmann and Hans Arnold (*Mitt. K. Materialprüfungsamt Gross-Lichterfelde West*, 1909, **27**, 470—473).—This method can be employed for alloys having the average composition Cu 40—50%, Sn 45—55%, and Sb 5%. About a gram of the alloy is dissolved in a mixture of nitric and tartaric acids, and the copper electrolytically deposited, any copper remaining in solution being subsequently precipitated in alkaline solution as sulphide. The filtrate is neutralised with sulphuric acid, acidified with oxalic acid, and antimony precipitated from the hot solution with hydrogen sulphide. The filtrate from the antimony is evaporated to a convenient volume, rendered slightly alkaline, and the tin precipitated as stannic acid by electrolysis, the deposition of 0·5 gram of tin requiring three to four hours. F. M. G. M.

Reducing Action of Alkali Formates on Some Inorganic Substances. Alexander Ch. Vournasos (*Compt. rend.*, 1910, **150**, 922—923. Compare this vol., ii, 286).—Reduction of boron nitride with sodium formate leads to the formation of amorphous boron with liberation of hydrogen, ammonia, and boron hydride. The same treatment reduces most metallic compounds to the free metal, and a method for the detection of small quantities of mercury is based on this fact. The substance is heated with dry sodium formate, and the evolved hydrogen burnt at a jet, the flame being allowed to impinge on porcelain, when a black stain of the metal is produced.

W. O. W.

Detection of Mercuric Chloride in Compressed Gun-cotton. Stephan P. Jannopoulos (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1910, **3**, 47).—Gun-cotton (30—40 grams) is made into a homogeneous paste

with distilled water, small pieces (15—20) of fine, bright, metallic copper wire stirred in with about 3 c.c. of concentrated hydrochloric acid, and the mixture left during several days. The copper wire is removed, washed successively with sodium hydroxide, water, alcohol, and ether, placed in a dry glass tube, and gently heated; a sublimate is produced which can be examined under a microscope for mercury, or, if preferable, iodine vapour is introduced, when crystals of mercuric iodide will be clearly visible. F. M. G. M.

Volumetric Estimation of Manganese with Potassium Permanganate. EDUARD DONATH (*Chem. Zeit.*, 1910, 34, 437).—The process given by Deiss (this vol., ii, 351) does not materially differ from that given by Schöffel and Donath in 1886. L. DE K.

The Precipitation of Iron and Copper with Nitrosophenylhydroxylamine in Quantitative Analysis. HEINRICH BILTZ and OTTO HÖDTKE (*Zeitsch. anorg. Chem.*, 1910, 66, 426—431. Compare Baudisch, this vol., ii, 76).—A 6% solution of ammonium "cupferron" (nitrosophenylhydroxylamine) precipitates ferric iron quantitatively. An excess of acid does not interfere with the precipitation. The separation of iron from nickel, aluminium, or chromium by this means is quantitative.

In precipitating copper, a large excess of mineral acid must be avoided. An acetic acid solution is the most suitable, and a double quantity of the reagent should be used. Cadmium and zinc do not interfere with the precipitation. Silver, mercury, lead, and tin are precipitated. Baudisch's method of separating iron and copper gives quantitative results. C. H. D.

The Volumetric Estimation of Uranium and Vanadium. E. DE MILLE CAMPBELL and CHARLES E. GRIFFIN (*J. Ind. Engin. Chem.*, 1909, 1, 661—665).—The various methods for estimating uranium and vanadium which have been described by Friedel and Cumenge, A. N. Finn, Fritchle, G. Edgar, and others are recapitulated and criticised. When uranium and vanadium are present in approximately equal amounts, the authors recommend the following procedure. The solution of the mixed metallic salts is rapidly heated to boiling with sulphuric acid in a tube containing a spiral of aluminium wire, and maintained at 100° until the grey colour of the solution shows that reduction is complete; the spiral is withdrawn, the solution cooled, and, after the addition of a little concentrated sulphuric acid, titrated with potassium permanganate. As the vanadium content was reduced in proportion to the uranium, the nearer the results came to the calculated figures and their uniformity increased; this was considered to be due to the tendency of the vanadium to oxidise in contact with air, and was to some extent prevented by the addition of ferric alum solution when the spiral was withdrawn. The application of the method to an ore analysis is described in the paper. F. M. G. M.

Improved Method for the Estimation of Titaniun. ALEXANDER GEMMELL (*Analyst*, 1910, 35, 198—202).—The sulphuric

acid solution, which should on no account contain more than 0·15 gram of titanium dioxide, is reduced in a conical flask, fitted with a rubber cork and Bunsen valve, by means of an alloy composed of ninety parts of zinc and ten parts of aluminium. When heated at 50°, the reduction is complete within five or eight minutes, provided the amount of titanium does not exceed 0·05 gram, but if over, a much longer time is required.

The liquid is now filtered as quickly as possible into a flask containing a solution of ferric sulphate and dilute sulphuric acid, the air having been swept out by means of a little solid sodium carbonate; as a precaution, a current of carbon dioxide may be passed over the funnel during filtration. The ferrous sulphate formed in the reaction is then titrated with standard permanganate.

Filtration through a tube containing small lumps of an alloy of magnesium and aluminium ("magnalium") also causes complete reduction, but its use is less convenient. L. DE K.

Vanadium and its Estimation. GEORGE AUCHY (*J. Ind. Engin. Chem.*, 1909, 1, 455).—A discussion as to whether the presence of vanadium imparts more valuable properties to steel than does that of other metals. The results of other workers are collected and expressed in "Quality Figures," which consist of the tensile strength, shock, and hardness figures of each sample summed up and expressed as a single figure; by this method, vanadium is shown to be, if anything, inferior to chromium, molybdenum, tungsten, and even to silicon unless the percentage of the latter exceeds 0·5%.

The various methods employed for the estimation of vanadium are considered, and one described in which the steel after solution in aqua regia is evaporated several times to dryness with hydrochloric acid and the operation subsequently repeated with sulphuric acid until hydrogen chloride is expelled, the residue treated with water and again evaporated several times to convert the vanadium completely into vanadium dioxide (V_2O_4), and finally titrated with potassium permanganate, the end point being indicated by the pink colour persisting after the liquid has had fifty to sixty vigorous shakings. The statement by Treadwell, that concentrated hydrochloric acid reduces vanadium pentoxide (V_2O_5) to a variable mixture of the lower oxides V_2O_4 and V_2O_3, is not corroborated by the author, except when the solutions have not been efficiently evaporated. F. M. G. M.

Volumetric Estimation of Antimony. EUGEN SCHMIDT (*Chem. Zeit.*, 1910, 34, 453—454).—The following existing processes are particularly recommended: (1) Titration with $N/100$-iodine in presence of sodium potassium tartrate and sodium hydrogen carbonate; the iodine should be added in very slight excess, and titrated back with thiosulphate. (2) Titration with $N/10$-potassium bromate in hydro chloric acid solution containing methyl-orange as indicator; th disappearance of the colour marks the end-point. (3) The direc titration with standard permanganate in hydrochloric acid solution.

L. DE K.

The Estimation of Caoutchouc as Tetrabromide. GEORG FENDLER (*Gummi Zeit.*, 1910, **24**, 931).—A discussion of the methods employed when caoutchouc is estimated as tetrabromide, with a criticism on the work and results obtained by Hübener. F. M. G. M.

Physico-chemical Estimation of the Ash of Wine. PAUL DUTOIT and MARCEL DUBOUX (*J. suisse Chim. Pharm.*, 1909, No. 26. Reprint, 7 pp.).—The authors having made a large number of experiments, propose the following formula: $(x\ 10^5 + \beta)(A + 20)/330 =$ % of ash, in which $x =$ the specific conductivity of the sample, and A the volume % of alcohol, whilst β is a factor depending on $x\ 10^5$. When the latter lies between 100 and 149 the value of $\beta = 0$, between 150 and 174 $\beta = 5$, between 175 and 199 $\beta = 9$, between 200 and 249 $\beta =$ 15, between 250 and 299 $\beta = 22$, between 300 and 399 $\beta = 30$, and between 400 and 500 $\beta = 40$. L. DE K.

Colour Reactions [for Fusel Oil, etc.] with Salicylaldehyde and Sulphuric Acid. HANS KREIS (*Chem. Zeit.*, 1910, **34**, 470).—The red coloration obtained by adding salicylaldehyde and sulphuric acid to an alcoholic solution of the higher alcohols (fusel oil) is not conclusive, since most ethereal oils also give the test.

These may, however, be removed to a great extent by diluting and salting out the original sample (such as artificial essences) before saponification and distillation. L. DE K.

Estimation of Phenol, Salicyl Alcohol, Salicylic Acid, and *p*-Hydroxybenzoic Acid as Tribromophenol Bromide. WILHELM AUTENRIETH and FRITZ BEUTTEL (*Arch. Pharm.*, 1910, **248**, 112—127).—Text-books still state that phenol in aqueous solution is estimated by precipitation as tribromophenol by an excess of bromine water, despite the fact that thirty years ago Benedikt showed that under these conditions the precipitate consists entirely of tribromophenol bromide [tribromophenyl hypobromite], $C_6H_2Br_3{\cdot}OBr$, m. p. 118° (Auwers and Büttner give the m. p. 131°, a value confirmed by the authors). The substance, which can be kept without loss of bromine for a long time over sulphuric acid in a vacuous desiccator, can be recrystallised unchanged from benzene, chloroform, or petroleum and carbon disulphide; other solvents convert it into tribromophenol. It is remarkably stable to boiling aqueous alkalis.

The estimation of phenol is performed as follows. The aqueous solution, about 0·2%, is placed in a large glass-stoppered bottle, and is slowly treated, at first with only gentle shaking, with so much saturated bromine water that the supernatant liquid is reddish-brown, and an appreciable amount of bromine vapour is present. After the mixture has been shaken vigorously for ten to fifteen minutes and kept in ice for four to six hours with frequent shaking, the precipitate is collected on a tared Gooch crucible, washed with bromine water, dried for three to four hours over sulphuric acid in a vacuous desiccator, and weighed as $C_6H_2OBr_4$; the result is accurate to within 3%.

Salicylic acid, salicyl alcohol, and *p*-hydroxybenzoic acid, all of

which yield tribromophenol bromide under the preceding conditions, can be estimated in a similar manner; in the case of salicylaldehyde the result is about 6% too low.

Aqueous solutions of *p*-cresol and bromine yield, under different conditions, mixtures of 3 : 5-dibromo-*p*-cresol, 3 : 5-dibromo-*p*-cresol bromide, $C_6H_2MeBr_2 \cdot OBr$, 3 : 5-dibromo-*p*-hydroxybenzyl bromide, and tribromophenol bromide. By the prolonged action, six to ten days, of an excess of saturated bromine water on its aqueous solution, *p*-cresol is ultimately converted into tribromophenol bromide; the yield, however, is only 77—88% of the theoretical. *o*-Cresol is not converted into tribromophenol bromide by bromine water. C. S.

Quinonoid Compounds. XXII. The Estimation of Quinones. RICHARD WILLSTÄTTER and RIKŌ MAJIMA (*Ber.*, 1910, 43, 1171—1175).—The authors have examined more fully the method formerly employed (Willstätter and Dorogi, Abstr., 1909, i, 535) for estimating quinones, which is based on that of Valeur (Abstr., 1900, ii, 57). When ethereal solutions are being dealt with, especially if they are impure, neither this method nor that of Wieland (this vol., i, 243) is satisfactory. The reaction between quinone and hydriodic acid reaches an equilibrium, so that it is necessary to have an excess of the latter in the ether during the titration of the liberated iodine. When the solution is coloured, a slight excess of dilute (*N*/10) thiosulphate is added, and the excess afterwards titrated back with iodine and starch. The ether used must be carefully purified, otherwise it liberates iodine itself, and produces a notable error. The concentrations of the solutions must be within certain limits.

The reaction with acidified potassium iodide proceeds rapidly enough with benzoquinone and toluquinone, but in the case of xyloquinone and thymoquinone it is so much slower that it is advisable to increase three-fold the excess of hydriodic acid. The reaction and titration must then be effected in an atmosphere of carbon dioxide to prevent the liberation of iodine by the oxygen of the air. R. V. S.

Detection of Inositol in Organic Products. G. MEILLÈRE and P. FLEURY (*J. Pharm. Chim.*, 1910, [vii], 1, 348—354).—The detection of inositol can only be accomplished by its isolation and the determination of its physical characters. The possibility of isolating it by precipitation with metallic salts, such as basic lead acetate, copper acetate, etc., is studied, and the following general method is suggested. The liquid is diluted to contain 0·5% of total sugars, calculated as dextrose. For liquids of animal origin, a mixture of lead and mercuric acetates is used as a preliminary defecating agent, and with vegetable infusions a solution of lead acetate, the solution in either case being first made slightly acid. The precipitate is filtered off, or removed by a centrifugal machine, and the filtrate neutralised. To it is added basic lead acetate, cadmium nitrate, and ammonia in succession. The precipitate so formed contains all the inositol with a proportion of sugars; it is collected, suspended in water, decomposed with hydrogen sulphide, and the excess of the latter removed. This filtrate is again treated with basic lead acetate and cadmium nitrate in succession.

This precipitate contains all the inositol, which can then be regenerated as before and purified by crystallisation from methyl alcohol. The preliminary defecation and the application of this general method to fermented liquors, animal fluids and plant juices, urines, etc., are discussed in detail in the original. T. A. H.

Estimation of Blood-Sugar. IVAR BANG, H. LYTTKENS, and J. SANDGREN (*Zeitsch. physiol. Chem.*, 1910, **65**, 497—503).—A comparison of the various methods in use for removing the proteins before the Bang method is employed for sugar estimation. The method recommended consists in general terms in extracting the blood thoroughly with alcohol, concentrating the alcoholic extracts, then treating with hydrochloric acid and blood-charcoal. The whole procedure, including the estimation, can be carried out in half an hour.
W. D. H.

Simple Method of Estimating Sugar in Blood. K. MOECKEL and E. FRANK (*Zeitsch. physiol. Chem.*, 1910, **65**, 323—329).—The method proposed by Bertrand (Abstr., 1907, ii, 136) for the estimation of reducing sugars can be employed to estimate the sugar in blood-plasma or -serum if all the protein matter is first removed by means of colloidal ferric hydroxide in the presence of a little magnesium sulphate, or, better, of sodium potassium tartrate. The authors give a table in extension of that published by Bertrand (*loc. cit.*). R. V. S.

The Digestion of Cellulose in the Domesticated Animals. IV. Simon and Lohrisch's Method for the Estimation of Cellulose. W. GRIMMER and ARTHUR SCHEUNERT (*Berl. Tierarztl. Wochenschrift*, 1910, **26**, Reprint).—When cellulose is treated with hot concentrated (50%) potassium hydroxide and subsequently with hydrogen peroxide, as described by Simon and Lohrisch in their method of estimating cellulose (Abstr., 1904, ii, 787), it does not remain unaffected, as these authors supposed, but a considerable proportion (25—40%) is dissolved. This loss again occurs if the treatment is repeated, so that the above method and the results obtained by means of it must be regarded as incorrect. R. V. S.

New Method for Estimating Cellulose. ROMAN DMOCHOWSKI and BERNHARD TOLLENS (*J. Landw.*, 1910, **58**, 1—20).—About 3 grams of the finely-powdered substance are boiled successively with 200 c.c. each of 1·25% sulphuric acid, water, 1·25% potassium hydroxide, and water in a Wattenberg dish (*J. Landw.*, 1880, **28**, 273). The liquid is then removed by means of a flat filter attached to a pump. The filter consists of a glass plate with grooves leading to a hole in the centre and connected on the other side with a tube; the plate is covered with a hardened filter paper, except with slimy substances, for which ordinary filter paper is used. Porcelain filters, with fine perforations, may also be employed.

The residue is next washed into a Gooch crucible with asbestos, and as much of the water as possible removed by suction. It is then transferred to a 100 c.c. beaker, and heated for an hour to about 80°

with nitric acid (D 1·15), being frequently stirred. The yellow substance is returned to the dish, and, after the nitric acid has been removed by suction, is boiled with water until no longer, or only slightly, yellow. Woody substances should be heated on a water-bath for half an hour with 2% ammonia, filtered, and boiled twice with water.

It is then filtered in a Gooch crucible, treated for half an hour with alcohol and ether, dried at 105—100° until the weight remains constant, ignited, and again weighed. The difference between the two weights multiplied by 1·1 gives the amount of cellulose.

N. H. J. M.

Employment of the New Method of Estimating Cellulose in Wood and the Materials Employed in the Paper Industry. ROMAN DMOCHOWSKI and BERNHARD TOLLENS (*J. Landw.*, 1910, **58**, 21—26).—Estimations of cellulose in wood, sulphite cellulose, and Swedish paper, etc., were made by the new method (preceding abstract) and by several other methods for comparison. In the case of wood, the results obtained by Henneberg's method were about 60% too high. The new method and that of Cross and Bevan show some agreement; it is considered, however, that the latter is less satisfactory, as no correction is made for loss of cellulose in the process.

N. H. J. M.

New Reaction for Glycuronic Acid. GUIDO GOLDSCHMIEDT (*Zeitsch. physiol. Chem.*, 1910, **65**, 389—393).—A trace of glycuronic acid dissolved in 0·5 c.c. of water and mixed with 1 or 2 drops of a 15% alcoholic solution of α-naphthol gives a deep emerald-green coloration on the addition of 3—4 c.c. of concentrated sulphuric acid, and this changes to deep blue or violet when diluted with water. The coloration is best seen when the aqueous liquid is poured carefully on to the concentrated acid. Glycuronic acid derivatives, for example, scutellarin, glycuron, acetylscutellarin, the phenylhydrazine, and *p*-bromophenylhydrazine derivatives of the acid, euxanthic acid, urochloralic acid, phenylglycuronic acid, and glycyrrhizinic acid, also give the same reaction.

A similar reaction is given by the glycuron present in normal urine.

J. J. S.

Assay of Anhydromethylenecitric Acid and of "Citarine" and "Helmitol." J. M. A. HEGLAND (*Pharm. Weekblad*, 1910, **47**, 418—422).—Anhydromethylenecitric acid, a condensation product of citric acid and formaldehyde having strongly acid properties, is assayed as follows: 0·408 gram of the product is heated in a flask with 10 c.c. of *N*-potassium hydroxide, 5 c.c. of water, and 6 c.c. of 3% hydrogen peroxide on the water-bath for one hour, and then just heated to boiling to decompose the excess of peroxide. When cold, 55 c.c. of water are added, and the liquid is titrated with *N*/10-hydrochloric acid, using phenolphthalein as indicator. Theoretically, 15·7 c.c. of acid are required to neutralise the excess of alkali.

"Citarine" (the sodium salt of the above acid) and "helmitol"

(its compound with hexamethylenetetramine) are best tested according to the directions given in Bayer and Co.'s pamphlet. L. DE K.

The Employment of Sodium Hydroxide and Barium Hydroxide in Formaldehyde Titrations. SÖREN P. L. SÖRENSEN (*Biochem. Zeitsch.*, 1910, **25**, 1—5).—In the presence of carbonates and phosphates, it is advisable to separate these acids by barium hydroxide and barium chloride before neutralising to litmus, and then titrating with barium hydroxide in presence of formaldehyde and phenolphthalein. If other essential substances are precipitated at the same time, then sodium hydroxide should be used for titration, and the error due to the presence of carbonates and phosphates is smaller. In titration of digests, barium hydroxide is preferable to sodium hydroxide in presence of carbonates and phosphates, except in cases when barium precipitates are produced, which interfere with the results. In solutions free from carbonate and phosphate, either reagent may be used for titration. S. B. S.

The Refraction of the Insoluble Fatty Acids of Butter Fat. G. DUMITRESCU and D. M. POPESCU (*Ann. Falsif.*, 1910, **3**, 149—153. Compare Abstr, 1907, ii, 314).—The authors consider that the refraction of the insoluble fatty acids of a sample of butter fat affords more certain evidence of sophistication than does the refraction of the butter fat itself, as the variation observed between the fatty acids from different butters is smaller than in the case of the fats. Forty-eight samples of butter examined gave refractometer numbers, at 40°, lying between 40·9 and 43·7, whilst the fatty acids from the same butters gave readings varying from 29·0 to 30·4; three other samples, however, yielded fatty acids showing a refractometer number of 31·1, but these samples are considered to be abnormal. The insoluble fatty acids of cocoanut oil gave a reading of 15·1; those of lard, 37·4, and those of beef fat, 37·4. W. P. S.

Estimation of Fat in Cocoa and Chocolate. ADOLF PROCHNOW (*Arch. Pharm.*, 1910, **248**, 81—88).—The author considers that rapid methods, such as those of Tschaplowitz (Abstr., 1906, ii, 404) and of Kirschner (*ibid.*, ii, 502), for the estimation of fat in cocoas are applicable only when very accurate results are not required. In view of recent determinations, the accepted average, 50%, of fat should be increased to 56%.

The adulteration of cocoa preparations with fats of vegetable origin can easily be detected, but not so the addition of animal fats. The detection of the latter by Neuberg and Rauchwerger's spectroscopic test, whereby cholesterol can be identified in the presence of phytosterol, appears to be untrustworthy, because the phytosterols, isolated by the author from two genuine cocoa butters and also from sesame oil and cotton-seed oil, give the spectrum characteristic of cholesterol. C. S.

The Reaction of Sesame Oil with Furfuraldehyde. P. N. VAN ECK (*Pharm. Weekblad*, 1910, **47**, 394—398. Compare *ibid.*, 1907, **44**, 1282)—In order to obtain the test for sesame oil, the

presence of β-hydroxy-δ-methylfurfuraldehyde or of furfuraldehyde is required. The following substances on treatment with hydrochloric acid yield the first-named aldehyde, and may, therefore, serve as new reagents: vanillin, heliotropine, anisaldehyde, and cinnamaldehyde. The following oils should be added to the list of those which do not give the reaction: *Oleum mucunae capitatae, oleum silybi Mariani, oleum lycopodei, oleum aleuriti,* and *oleum staphidis agriae.*

A well-known test for pyrogallol is the violet-red coloration obtained on boiling with hydrochloric acid and adding a little vanillin. The latter may, however, be replaced by one of the other three reagents.

L. DE K.

Aromatic Nitro-derivatives, particularly Nitrophenols, as Precipitants for Alkaloids. LEOPOLD ROSENTHALER and P. GÖRNER (*Zeitsch. anal. Chem.*, 1910, **49**, 340—358).—The action of sixteen representative nitro-compounds of the phenol type on thirty-four alkaloids has been studied, and the results are tabulated. In several cases characteristic precipitates were obtained, and micro-illustrations of some of these are shown.

L. DE K.

Colour Reactions of Adrenaline and Allied Bases. ARTHUR J. EWINS (*J. Physiol.*, 1910, **40**, 317—326).—The colour reactions of adrenaline produced by iodine, mercuric chloride, or di-iodate are due wholly or in part to oxidation, and a new reagent acting in the same way, namely, potassium persulphate, gives a similar red colour, owing to the same cause. It is more sensitive than the others; other bases (the amino-base corresponding with adrenaline, dehydroxyphenylethylamine, the corresponding methyl, ethyl and propylamino-bases, and aminoacetopyrogallol) gave the same reaction. Those of the type aminoacetocatechol do not.

W. D. H.

Estimation of "Ferripyrine." A. ASTRUC and J. BOUISSON (*J. Pharm. Chim.*, 1910, [vii], 1, 395—397).—When "ferripyrine" is neutralised with sodium or potassium hydroxide, using phenolphthalein as indicator, the iron is precipitated as ferric hydroxide, and a solution of antipyrine is obtained. The amount of antipyrine in this solution may be estimated by titration with iodine, as described by Bougault (Abstr., 1899, ii, 193), or by the use of picric acid, as suggested by Astruc and Pégurier for pyramidone (Abstr., 1905, ii, 778). In the latter case, sodium hydroxide must be employed for the initial neutralisation.

T. A. H.

Separation of Creatinine from Meat Extracts. KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 426—434).—The following method is described for the separation of creatinine from meat and other extracts, as it is sometimes important to prove that the coloration obtained with alkaline picric acid (Jaffé's reaction) is actually due to the presence of creatinine in a given extract. A quantity of the extract is dissolved with water and treated with lead acetate in excess, the precipitate formed being separated by filtration, and the excess of lead then removed from the filtrate by evaporation after the addition

of hydrochloric acid and alcohol. The lead-free solution is next treated with 20% sodium hydrogen sulphide solution and 13% copper sulphate solution, boiled, cooled, and filtered. After removing sulphurous acid and copper from the filtrate, the latter is evaporated and extracted with alcohol, the alcoholic solution obtained being in turn evaporated. The resulting syrup is dissolved in dilute sulphuric acid, and the solution is treated with phosphotungstic acid solution. After the lapse of two days, the precipitate is collected on a filter, washed, and then decomposed by boiling with a slight excess of barium hydroxide. The mixture is passed through a filter, the excess of barium is removed from the filtrate by evaporation with sulphuric acid, the barium-free solution is evaporated, and the residue extracted with alcohol. The alcoholic solution is evaporated, the residue is dissolved in water, lead hydroxide and an excess of hot alcohol are added, the solution is filtered after the lapse of several hours, and the excess of lead is removed from the filtrate as sulphide. The solution is then evaporated, the crystalline residue is dissolved in 1·2% picric acid solution, and allowed to crystallise. The creatinine picrate is collected on a filter, and the filtrate evaporated under reduced pressure, a further small quantity of creatine picrate thus obtained being added to the main bulk. After decomposing the picrate with hydrochloric acid and extracting the picric acid with toluene, the creatine hydrochloride solution is evaporated until crystallisation commences. The mass of crystals is treated with a mixture of 1 part of acetone with 2 parts of alcohol, and collected on a filter, the filtrate being then evaporated in order to obtain a small quantity of creatine hydrochloride passing into solution. The crystals are dried at a temperature of 100° and weighed. A sample of meat extract examined yielded 4·5% of creatine hydrochloride. The method may be applied to mixtures of meat and yeast extract, but, in this case, larger quantities of the substance must be employed. W. P. S.

Estimation of Morphine. RUDOLF GOTTLIEB (*Arch. exp. Path. Pharm.*, 1910, **62**, 430).—It is pointed out that Winterstein's recent criticisms (this vol., ii, 363) on Rübsamen's method are based on a misunderstanding of certain points in the technique. W. D. H.

Estimation of Morphine, Narcotine, and Codeine in Opium and its Galenical Preparations. P. VAN DER WIELEN (*Bull. Sci. Pharmacol*, 1910, **17**, 59—63).—For the estimation of the morphine, the process given in the Dutch Pharmacopœa is followed; this is essentially the same as the method given in the French Codex.

For the estimation of the narcotine and codeine, the following process is recommended. Ten grams of opium are boiled with 100 grams of alcohol (70° French) in a reflux apparatus for an hour, and any loss in alcohol is restored. In 5 grams of the filtrate the extract is determined. Suppose the solution contains p% of extract, then the total quantity of the alcoholic solution is 10,000/100-p grams, and 3 grams of opium correspond with 3000/100-p grams of the alcoholic solution. This quantity is evaporated in a porcelain capsule to 3 c.c., which are then transferred to a flask, the capsule being washed three

times in succession with 2·5 c.c. of water; 90 c.c. of ether are added, and, after shaking, 5 c.c. of 10% sodium hydroxide are introduced. After three hours interval, with occasional shaking, 3 grams of gum tragacanth are added, and 75 grams of the clear ethereal solution evaporated to dryness. The residue is then dissolved by warming with 4 grams of alcohol (90° French). After twenty-four hours, the crystals of narcotine are collected, washed with 5 c.c. of alcohol, dried, and weighed. As narcotine is not quite insoluble in alcohol, a correction of +0·016 gram must be applied.

The filtrate containing the codeine is diluted with 10 c.c. of water, and then evaporated to 10 c.c. The resinous matters separate, and, after twenty-four hours the solution is filtered. Ten c.c. of *N*/100-hydrochloric acid are added, and the excess of acid is titrated with *N*/100-sodium hydroxide, using hæmatoxylin as indicator; 1 c.c. of acid = 3·17 mg. of codeine.

For the estimation of narcotine and codeine in extract of opium, 3 grams of the sample are dissolved in 5 c.c. of water and shaken with ether, etc., as just directed. When dealing with tinctures or laudanum, 30 c.c. of the sample are evaporated to expel the alcohol, and further treated in the same manner.

An alcoholic extract of opium seems to contain more alkaloids than an aqueous one. L. DE K.

The Tryptophan-aldehyde Reaction. GEORGE W. HEIMROD and PHŒBUS A. LEVENE (*Biochem. Zeitsch.*, 1910, **25**, 18—23).—Hehner's test for formaldehyde (tryptophan-containing protein, formaldehyde, ferric chloride, and concentrated sulphuric acid) is characteristic for this aldehyde. A similar reaction is, however, given with other aldehydes if, before the addition of the sulphuric acid, the mixture is warmed with a little phosphoric acid. The colours given with indole and skatole are not so marked as those given with tryptophan. S. B. S.

Estimation of the Pharmacological Activity of the Dried Leaves of Digitalis purpurea. OSCAR SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1910, **62**, 305—328).—The therapeutic use of digitalis is uncertain, and various methods for estimating the activity of preparations, such as lethal dose, effect on blood-pressure, etc., have been from time to time proposed. These are discussed in full, as well as the precautions necessary to obtain extracts as nearly alike in concentration as possible. The method for standardising adopted is the effect produced on the frog's heart, and experiments with various preparations of the leaves are described. W. D. H.

Hæmolysis as a means of Detecting Saponin in Beer, Aerated Waters, and Wine. ARNALDO RUSCONI (*Boll. Soc. Med.-Chir. Pavia*, 1910, Feb. 4).—The saponins, which are often added to beer and other beverages for the purpose of head-formation, all exert a greater or less hæmolytic action. Normal red wines contain a factor inhibitive of hæmolysis by saponin, a factor which consists neither of the tannin nor of the colouring matter, but which is susceptible of fixation by gelatin or albumin. The method of testing is as follows.

The liquid to be tested is rendered isotonic or somewhat hypertonic to the red blood-corpuscles by the addition of 2% sodium citrate solution. The blood-corpuscles are separated and washed in the ordinary way, and are then taken up, to the extent of 5%, in 1% sodium chloride solution. Two c.c. of this globule suspension, together with 5 drops of the liquid treated as above, are kept in a thermostat for three hours, then in the open air for twelve hours, after which the liquid is tested to ascertain whether hæmolysis has occurred. With beer one part of saponin per 10,000 can be detected, whilst with aerated waters the sensitiveness of the test is 1 in 400,000. T. H. P.

A New Protein Colour Reaction. Organ-peptides. W. Arnold (*Bull. Acad. Sci. Cracow*, 1910, *A*, 56—60, 61—64).—The protein of the crystalline lens, when dissolved in water either before or after purification by repeated precipitation with ammonium sulphate, gives the following reaction: a few drops of a 4% solution of sodium nitroprusside and then of ammonia produce an intense purple colour, which is discharged by acetic acid. Various other tissue proteins give the reaction in varying degrees of intensity. The proteins of egg-white do not, unless previously subjected to peptic digestion. Keratin belongs to this group also. A third group of proteins (ovomucoid, mucin, casein, and the proteins of blood-plasma) do not give the reaction even after digestion. Various amino-acids investigated also give a negative result.

The positive result in organ proteins is believed to be due to admixture with hydrolysed products of protein, which are called organ-peptides. These are considered to be of physiological importance, and are more abundant in the tissues of warm-blooded than in those of cold-blooded animals. W. D. H.

Detection of Albumin in Urine. Y. Oguro (*Chem. Zentr.*, 1910, i, 63; from *Zeitsch. expt. Path. Ther.*, 1909, **7**, 349—351).—I.—Five c.c. of urine are acidified with acetic acid and mixed with 1 c.c. of tincture of iodine (one part of iodine, ten parts of alcohol), and the brown liquid is then decolorised by cautiously adding saturated solution of sodium hydrogen sulphite. An opalescence or a flocculent precipitate shows the presence of albumin; traces will take a few minutes to form.

II.—The tincture of iodine is first decolorised with the acid sulphite, filtered, and then used as a reagent for albumin. L. de K.

Rapid Estimation of Albumin in Urine. Aufrecht (*Chem. Zentr.*, 1909, ii, 2204; from *Deut. med. Woch.*, 1909, **35**, 2018—2019).—A modification of the Esbach albuminometer. The precipitate formed on addition of 3 c.c. of the picric acid solution to 4 c.c. of the urine (acidified, if necessary, with acetic acid) settles in the drawn out and graduated part of the tube when submitted to a two minutes' centrifugal action.

Propeptone may be estimated by heating 4 c.c. of the urine in a test-tube. The filtrate is then introduced into the apparatus, diluted to the mark with absolute alcohol, and centrifugalised. The volume of the precipitate equals % of propeptone. L. de K.

General and Physical Chemistry.

The Refraction and Dispersion of Argon and Redeterminations of the Dispersion of Helium, Neon, Krypton, and Xenon. CLIVE CUTHBERTSON and MAUD CUTHBERTSON (*Proc. Roy. Soc.*, 1910, *A*, **84**, 13—15. Compare Abstr., 1909, ii, 105).—The mean of seven experiments gave 1·00028230 for the refractive index of argon for the wave-length 5461. The dispersion observed between the wave-lengths 6438·5 and 4799·9 (7 lines) agreed with the formula $\mu - 1 = c/(n_0^2 - n^2)$, in which c was $9{\cdot}43264 \times 10^{27}$ and n_0^2 $17008{\cdot}9 \times 10^{27}$. Improvements in the source of light (use of the arc with poles of cadmium-silver and lithium-silver alloys) made it worth while to repeat the former measurements for the dispersion of the other rare gases, and the values of n_0^2 now found agreed to within 2% with the former determinations. A table of the constants for the five rare gases is given. F. S.

Molecular Dispersion of *cyclo*Pentadiene. A Correction. KARL AUWERS and FRITZ EISENLOHR (*Ber.*, 1910, **43**, 1545. Compare this vol., ii, 367).—The theoretical value for the molecular dispersion of *cyclo*pentadiene is 0·87 (not 0·46), and this agrees with the experimental value, so that the compound does not show exaltation. J. J. S.

Wave-length Measurements in the Visible Region of the Arc Spectrum of Welsbach's Elements, Aldebaranium and Cassiopeïum. JOSEF EDER and EDUARD VALENTA (*Zeitsch. anorg. Chem.*, 1910, **67**, 102—106).—The two components of ytterbium, aldebaranium and cassiopeïum, have been examined in the arc. Both elements give bright characteristic lines in the region from green to red, tables of which are given. C. H. D.

Positive Band Spectrum of Nitrogen and its Variation with Temperature. ERNST ANGERER (*Ann. Physik*, 1910, [iv], **32**, 549—576).—The spectra of the positive glow emitted by Geissler tubes containing nitrogen at the ordinary temperature and at the temperature of liquid air have been compared. Special arrangements were made to ensure that the conditions of discharge should be as nearly as possible the same at the two temperatures.

In general, the spectrum obtained at the lower temperature is much less intense than that emitted at the ordinary temperature. In the case of certain bands and lines, however, the lowering of temperature is not accompanied by any appreciable alteration in the intensity of the emitted light. Similar experiments with hydrogen and helium have shown that the spectrum of these gases is unaltered by change of temperature. On the other hand, argon appears to behave in the same way as nitrogen.

The wave-lengths of the nitrogen lines and bands are recorded in detail. H. M. D.

Dispersion in the Electrical Spectrum of Petroleum. N. OBOLENSKY (*Physikal. Zeitsch.*, 1910, **11**, 433—440).—The dispersion in the electrical spectrum of Caucasian petroleum has been examined by the method used by Colley (Abstr., 1908, ii, 909). Measurements of the refractive indices for electrical waves of different wave-lengths are recorded, and curves are drawn which show the dependence of the refractive index on the wave-length. These curves indicate the resistance of a large number of dispersion bands. The well-defined band between 332 and 335 mm. (half wave-length in air) is also found in the electrical spectrum of toluene and acetone, and its presence in the spectrum of petroleum containing naphthenes is considered to afford further evidence in favour of the view that this band is due to the methyl group.

With rise of temperature, this dispersion band appears to be displaced in the direction of greater wave-lengths. The variation of the refractive index of petroleum with temperature is only in approximate agreement with the requirements of the Clausius-Mossotti formula. H. M. D.

Absorption Spectra of Nitrates. KONRAD SCHAEFER (*Zeitsch. wiss. Photochem.*, 1910, **8**, 212—234, 257—287).—A detailed examination has been made of the absorption due to the NO_3 group in metallic and organic nitrates. The experimental data show that these two series of compounds are sharply distinguished from one another by their absorption spectra. In the case of solutions of metallic nitrates, the absorption spectrum is almost independent of the nature of the metal and of the degree of ionisation of the salt. This specific character of the absorption is, moreover, not confined to solutions of the metallic salts, for it is found that solid potassium nitrate has the same spectrum as is shown by its dilute solutions.

The behaviour of organic nitrates is quite different. From the examination of methyl, ethyl, amyl, and allyl nitrates, it appears that the organic nitrates show only general absorption. Although these substances were examined under different conditions in the liquid and vapour form, and also dissolved in various solvents, there was no evidence of selective absorption. The observations are discussed from the point of view of the theories of Stark and Hantzsch.

H. M. D.

Absorption Spectra of Potassium Cobaltous Thiocyanate in Organic Solvents. JAN VON ZAWIDSKI (*Chem. Zentr.*, 1910, i, 1426—1427; from *Chemik Polski*, 1910, **10**, 49).—Potassium cobaltous thiocyanate, $K_2Co(CNS)_4$, is soluble in many organic solvents, but not in hydrocarbons and alkyl halides. The solutions are dark blue, and the characteristic absorption spectrum is independent of the solvent. The solvents examined include alcohols, aldehydes, ketones, acids, nitrobenzene, esters, nitriles, cyanohydrins, and thiocyanates. The spectrum is therefore due to the complex $Co(CNS)_4$, being independent of the ionising power of the solvent. The complex is broken up by water and formamide, and the pink colour of cobaltous salts is then obtained. C. H. D.

Absorption Spectrum of the Three Xylenes in the Ultra-violet. WILHELM MIES (*Zeitsch. wiss. Photochem.*, 1910, 8, 287—291. Compare Abstr., 1909, ii, 776).—In order to ascertain the influence of the relative position of the methyl groups on the ultra-violet absorption spectrum, the author has investigated the vapours of *o*- and *m*-xylene by the same method as that previously used for *p*-xylene. The absorption of *m*-xylene is considerably weaker than that of the para-compound, and contains only one series of bands instead of the two exhibited by *p*-xylene. The absorption of *o*-xylene is still smaller, and the photographs afford no evidence of any definite series of bands. In regard to the position of the heads of the bands, *p*-xylene approximates to *o*-xylene more closely than to the meta-compounds. The heads of the most intense bands are at the following wave-lengths: para $\lambda = 2722{\cdot}5$, meta $\lambda = 2721{\cdot}5$, and ortho $\lambda = 2723$. The relative behaviour of the three xylenes in the liquid state is similar to that found by the examination of the vapours. H. M. D.

Evidence of the Nature of Chemical Ring-compounds on the Basis of Ultra-violet Fluorescence. HEINRICH LEY and W. GRÄFE (*Zeitsch. wiss. Photochem.*, 1910, 8, 294—300).—The fluorescence spectrum of α-naphthylamine consists of a single broad band reaching from $\lambda = 1920$ to $\lambda = 2690$. On addition of an equimolar quantity of hydrogen chloride to an alcoholic solution of the amine, the fluorescence band is reduced in intensity and displaced slightly towards the ultra-violet; at the same time a new band makes its appearance in the region $\lambda = 2700$—3100. With increasing relative proportions of acid, this band is resolved into a series of nine bands which closely resemble the fluorescence bands of naphthalene. These bands are attributed to α-naphthylamine hydrochloride, and the close similarity between the spectrum of the hydrochloride and that of naphthalene is attributed to the existence of a similar condition in the ring structure of the two compounds. The entirely different fluorescent spectrum of the free base is attributed to the effect of the presence of the unsaturated nitrogen atom.

The absorption spectra of α-naphthylamine and its hydrochloride are also quite different, but the latter resembles that of naphthalene.

H. M. D.

Rotation Dispersion. I. Influence of the Solvent on the Rotation of Ethyl Tartrate and of Menthol. HERMANN GROSSMANN (*Zeitsch. physikal. Chem.*, 1910, 73, 148—162. Compare Abstr., 1909, ii, 713; this vol., ii, 372).—The optical rotation of solutions of ethyl tartrate in a large number of solvents, including all the liquid halogen derivatives of methane and ethane, certain alcohols, benzene hydrocarbons, and a number of their derivatives, has been measured for light of different wave-lengths at 20°, and the results are represented graphically and also in tabular form. The magnitude of the rotation varies enormously with the nature of the solvent. In those solvents in which the specific rotation in the red is higher than that for the pure ester, the dispersion curve rises from red to blue, whilst for such solvents as tetrachloroethylene and tetrachloroethane,

in which the specific rotation is less than that of the pure liquid, the dispersion curve falls from red to blue.

A progressive increase in the number of chlorine atoms in methane and ethane regularly lessens the specific rotation towards the right until the system becomes lævorotatory, but beyond a certain point the rotation towards the right increases with an increase in the number of chlorine atoms.

The entrance of the nitro- and amino-groups into benzene greatly increases the rotation to the right in these solvents; the effect of the aldehyde and primary alcohol groups is also considerable, whilst other substituents, such as a single halogen or methyl group, have a slight diminishing effect.

In solvents which have only a slight effect on the specific rotation, the dispersion curve shows a maximum, as in the case of the ester itself. The greatest specific rotation was observed in pyridine, quinoline, and furfuraldehyde.

Measurements were made with 6, 15, and 30 grams of the ester in each solvent, and thus information has been gained as to the effect of change of concentration of the solvent on the rotation. In solvents in which the ester is strongly dextrorotatory, the specific rotation-temperature curve tends to fall as the concentration increases, whilst in lævorotatory solutions it rises in the same circumstances. Quinoline and tetrachloroethane are exceptional, inasmuch as in the former case there are indications of a maximum, in the latter case of a minimum, in the rotation-concentration curve. For acetone a maximum, and for xylene and ethylene chloride minima, have actually been observed.

When menthol is used as optically active substance, change in concentration of the solvent has much less influence, and the course of the dispersion curves is very similar in all solvents. G. S.

Chemical Effect of Ultra-violet Light on Gases. Oxidising Actions. Combustion of Cyanogen and Ammonia; Synthesis of Formic Acid. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **150**, 1327—1329. Compare this vol., i, 349).—No paracyanogen is formed when cyanogen is exposed to ultra-violet light in presence of oxygen, the gas becoming completely oxidised to carbon dioxide and nitrogen. Under the same conditions, ammonia is first decomposed into its elements, the hydrogen then becoming oxidised to water; a mixture of hydrogen and oxygen, on the other hand, is unaffected by ultra-violet light.

On exposing a mixture of acetylene (1·60 c.c.) and oxygen (2·72 c.c.) for four hours at a distance of 4 cm. from a quartz-mercury lamp (220 volts), a mixture was obtained consisting of carbon dioxide (0·57 c.c.) and carbon monoxide (0·88 c.c.), together with formic acid, unaltered oxygen, and acetylene. A mixture of ethylene and oxygen in the same way gave carbon dioxide, formic acid, and carbon monoxide if the amount of oxygen was limited. W. O. W.

Eder's Solution. II. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1910, **8**, 197—211, 237—256. Compare Abstr., 1909, ii, 283; this vol., ii, 115).—Further experiments have been made relating to the

influence of iron and oxygen on the photochemical sensitiveness of Eder's solution. The sensitiveness is very largely dependent on the purity of the mercuric chloride and the ammonium oxalate which are used in the preparation of the solution. The active impurity is iron, and experiments with solutions containing very small quantities of ferric chloride show that the photochemical sensitiveness is proportional to the iron content. These observations lead to the conclusion that a solution of mercuric oxalate which is completely free from iron would not exhibit any photochemical effect.

Further measurements of the rate at which mercurous chloride is precipitated from an active solution show that the previously-observed period of induction corresponds with the time required for the disappearance of the free oxygen dissolved in the solution. With decreasing iron concentration, the retarding influence exerted by oxygen increases very rapidly. On account of this variable influence exerted by oxygen, the use of Eder's solution for exact actinometric measurements cannot be recommended.

Spectrophotographic observations show that Eder's solution has a specific absorption spectrum in the ultra-violet region. It is shown, however, that this spectral absorption is not necessarily accompanied by a special photochemical extinction. H. M. D.

The Phosphorescence Produced by α- and β-Rays. E. MARSDEN (*Proc. Roy. Soc.*, 1910, **83**, *A*, 548—561).—Continuous bombardment of a zinc sulphide screen by α-particles produces a marked and rapid diminution of the luminosity, but only a slight reduction in the number of scintillations. The luminosity was diminished by rise of temperature (6% less at 100° than at 15°), but no marked alteration occurred at solid carbon dioxide and liquid air temperatures. Infra-red radiation diminished the luminosity but slightly. Spectroscopic photographs of the luminosity showed a band toward the red, and another towards the blue end of the spectrum, and the intensity of the former decayed relatively to the latter with continued bombardment. An estimate of the fraction of the energy converted into light was effected by a differential air calorimeter, measurements being taken with the zinc sulphide covered with black paper and not covered. 1·5% of the total energy appeared as light energy. Willemite also underwent a reduction of luminosity with long bombardment, but not so rapidly as zinc sulphide, whereas the reduction in barium platinocyanide was very rapid, falling to half value in eight minutes when exposed to 5×10^7 α-particles per second per sq. cm. The phosphorescence of these materials under β-rays, and its decay after cessation of the exciting cause were also examined. F. S.

Theory of the Luminosity Produced in Certain Substances by α-Rays. ERNEST RUTHERFORD (*Proc. Roy. Soc.*, 1910, **83**, *A*, 561—572. Compare preceding abstract).—The theory proposed is that "active centres" exist in a substance rendered luminous by α-rays uniformly distributed among the inactive molecules, and that a scintillation is the result of the dissociation of a number of these active centres lying in the path of the α-particle, and that, after being

once struck, each active centre becomes ineffective in producing light. This explains the reduction of luminosity by bombardment, and the fact that the number of scintillations only slightly diminishes (Marsden). The experimental curves obtained are found to agree well with the theoretical curves worked out from this theory. According to it the diameter of the cylinder of material affected by the passage of a single α-particle can be calculated from the observed curves of decrease of luminosity by continued bombardment, and it is shown that whereas for zinc sulphide and willemite the diameter is 1·3 and 2·5 ($\times 10^{-7}$ cm.), which is somewhat larger than the diameter of a molecule, it is very much greater for barium platinicyanide, namely, $1\cdot6 \times 10^{-5}$. This excludes an earlier suggestion that the scintillations of zinc sulphide are due to the mechanical cleavage of small crystals.

F. S.

Magnetic Line-Spectrum of β-Rays. OTTO VON BAEYER and OTTO HAHN (*Physikal. Zeitsch.*, 1910, 11, 488—493).—If the β-rays which are exponentially absorbed are homogeneous, they should, after passage through two slits in a suitable magnetic field, be deviated uniformly, and give a sharp image of the slit when received on a photographic plate, as is well known to be the case for the α-rays. If two or more homogeneous types are present, there should be received on the plate a magnetic line-spectrum consisting of two or more sharp images, the slower rays being the more easily deviated. In such a photograph taken with the active deposit of thorium, two sharp lines, due to the β-rays of thorium-A and thorium-D respectively, could be seen, and also three others, two due to very slow β-rays too feebly penetrating to be distinguishable from α-rays in absorption measurements, and a third to rays slightly faster than those of thorium-A. For radium-E_2, one not very sharp line only was observed. For mesothorium-2, a broad band, tailing off, due to slightly deviated β-rays, was seen, agreeing with an earlier view that the radiation is complex. In addition, four sharply separated lines due to very soft β-rays were observed. A radio-thorium preparation showed in addition to the lines due to thorium-A and thorium-D, another due to thorium-X, still more strongly deviated (compare following abstract). These results show that β-rays are expelled with definite and characteristic velocity like the α-rays, and that probably each β-ray product emits only one group of typical β-rays. F. S.

A New β-Radiation from Thorium-X; Analogies in the Uranium and Thorium Series. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1910, 11, 493—497. Compare preceding abstract). —It is stated that a radium preparation has been obtained showing a gradual growth of radiation to double the maximum reached after a month, and this is regarded as evidence for the existence of a new product, radium-X, produced from radium and giving the soft β-rays ascribed to that substance, but no separation has yet been effected. From analogies between the uranium and thorium series, it was considered probable that thorium-X should give an absorbable β-radiation. In a series of experiments, thorium-X was freed as

completely as possible from thorium-*A* and thorium-*B*. The latter was removed by boiling the solution with charcoal, and the former by igniting the evaporated filtrate. A very feebly penetrating β-radiation always remained with the thorium-*X* so purified, and it was calculated that it was absorbed about three times as readily as the β-radiation of thorium-*A*. In the course of time, as thorium-*A* and thorium-*B* were regenerated, the β-rays showed a continuous rapid increase of penetration power. In conclusion, various analogies between the uranium and thorium disintegration series are elaborated.

F. S.

The Total Ionisation Produced in Different Gases by the Cathode Rays Ejected by *X*-Rays. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1910, *A*, **84**, 16—24).—The experiments were made to test whether, as appears probable, the energy necessary to make an ion from any given atom is independent of the nature of the ionising agent or of its penetrating power. The ionisations in various gases and vapours at low pressures produced by a beam of *X*-rays of known intensity were measured when screens of cardboard coated with gold leaf on one side were interposed in the path of the beam. By subtracting the effect when the gold-coated side was towards the ionisation chamber from that when the opposite was the case, the ionisation produced by the cathode radiations from the gold only could be found. Owing to the feeble penetrating power of these radiations, they are entirely absorbed in the gas, even at low pressure, and for gases containing atoms no heavier than oxygen, the ionisation was independent of the pressure. In heavier gases containing bromine and chlorine, the ionisation increased with pressure, which is considered to be due to the gold generating soft *X*-rays in addition, which are relatively much more readily absorbed by heavy gases. This could in most cases be corrected for. The results showed that the relative total ionisation produced by the cathode rays in different gases was similar to what Bragg had found for the same gases exposed to α-rays. It is deduced from this that the energy necessary to ionise an atom is the same for the cathode ray as for the α-ray, and that the path of the cathode ray in different gases is inversely as the sum of the square roots of the atomic weights of the constituent atoms of the molecule. A summary of other work bearing on the question of the total energy required to produce an ion is given at the end of the paper.

F. S.

On Secondary Homogeneous *X*-Radiation. J. C. CHAPMAN and S. H. PIPER (*Phil. Mag.*, 1910, [vi], **19**, 897—903).—A primary beam of *X*-rays of a degree of hardness sufficient to excite homogeneous copper radiation without directly stimulating the homogeneous silver rays, produced only homogeneous copper radiation when caused to fall on a plate composed of an alloy of one part of copper to two parts of silver. The experiment points to the conclusion that the homogeneous radiations are not produced by the electrons ejected by the impact of *X*-rays from the atoms, but from the vibration of the atoms from which the electrons are ejected. An experiment to see

whether secondary X-radiation persisted, like phosphorescence, after the exciting cause ceased, gave negative results. From copper and zinc it cannot continue at $\frac{1}{250}$th of its initial strength $\frac{1}{3000}$th second after the exciting cause ceases. F. S.

Radium-*D* and its Products of Transformation. GEORGE NICOLAEVICH ANTONOFF (*Phil. Mag.*, 1910, [vi], **19**, 825—839).—The period of radium-*D* has been determined by a new method, in which the number of α-particles emitted from radium-*F* produced after the lapse of a known time (120 to 320 days) from a known initial quantity of emanation, left to decay in a sealed tube, has been counted by the scintillation method. The mean of five results gives 16·5 years for the period of half-change with a probable accuracy of $\pm 0·5$ year. The existence of two short-lived products (radium-E_1 and -E_2) between radium-*D* and -*F* has been disproved. Only one, radium-*E*, exists, giving β-rays, with a half-period of five days. A piece of platinum foil was exposed to the emanation from 150 mg. of radium bromide for a day, and the active deposit dissolved off and evaporated in a watch-glass. A few hours after the exposure, it is practically pure radium-*D*. β-Radiation, due to the formation of radium-*E*, was generated regularly and normally with the five-day period. Radium-*E* separated from radium-*D* by precipitating the latter with barium sulphate decayed exponentially with the same period. In another method, radium-*D* was volatilised from radium-*E* in a blowpipe flame. The absorption of the β-rays of radium-*E* is exponential, the value of the absorption-coefficient for aluminium being $43(\text{cm.})^{-1}$, and for copper, $164(\text{cm})^{-1}$. From old solutions of radium, radium and radium-*D* are completely removed by precipitation with barium sulphate, whereas radium-*E* and radium-*F* are left in the solution. F. S.

The Estimation of Radium. STEWART J. LLOYD (*J. Physical Chem.*, 1910, **14**, 476—481).—The effect of the addition of various reagents on the measurement of the radium in a radium-barium solution by means of the usual emanation method has been investigated. Only in the presence of hydrochloric or nitric acids is the emanation fully evolved. Sulphuric acid and sodium carbonate, which precipitate the barium and radium, diminish the amount of emanation evolved very markedly. The production of other precipitates in the solution did not cause much effect. Stirring and heating the precipitate of barium sulphate after its formation facilitates greatly the subsequent evolution of emanation, due to the radium being released when the precipitate recrystallises. Some time after the precipitate of barium sulphate has been formed in a radium-containing solution, the latter again recovers its initial power of evolving emanation. F. S.

The Constant of Uranium-*X*. FREDERICK SODDY and ALEXANDER S. RUSSELL (*Phil. Mag.*, 1910, [vi], **19**, 847—851).—The decay curves of both the β- and γ-rays of the uranium-*X* preparations from 45 kilograms of uranyl nitrate have been examined over a period of 230 days, in which time the radiation is reduced to 0·15% of the initial value. Both radiations were found to decay normally at exactly the

same rate, the value of the radioactive constant, λ, of uranium-X being $0{\cdot}0282(\mathrm{day})^{-1}$. The period of average life is 35·5 days, and of half-change, 24·6 days. The latter values are about 10% greater than those previously in use. Some of the preparations used showed a more rapid decay of the β-rays for the first ten days ($\lambda = 0{\cdot}033$ to $0{\cdot}029$), but the effect is ascribed to possible errors, such as absorption of moisture from the air. Both β- and γ-rays decay normally to zero. Some preparations were examined up to fourteen months from preparation, until the β-radiation was only $\frac{1}{100,000}$th of its initial value. F. S.

Rate of Decay of the Radioactivity of Polonium. JOHN WILLIAM WATERS (*Phil. Mag.*, 1910, [vi], **19**, 905—906).—The rate of decay of a specimen of polonium five years old, during which time the activity would be reduced to one-thousandth part of the initial, proved to be normal with a period of half-change of one hundred and forty-eight days. This is so near the rate found by Mme. Curie for freshly prepared material, that it is probable that the product of the change is not itself radioactive. F. S.

Table of Radioactive Elements. HEINRICH GREINACHER (*Zeitsch. Elektrochem.*, 1910, **16**, 267—269).—A table of the thirty known radioactive elements, containing the time in which their activity is halved, the kind of rays given out, the penetration and velocity of the α-rays, and the absorption-coefficients of the β-rays for aluminium and of the γ-rays for lead. T. E.

Radioactivity of Minerals. I. CORNELIO DOELTER and HEINRICH SIRK (*Monatsh.*, 1910, **31**, 319).—Green zircons from Ceylon were found to be appreciably radioactive, but the red and brown varieties examined were not. A crystal of Norwegian monazite, not perfectly pure, was active, but it is probable that this mineral owes its activity to isomorphous inclusions of thorium phosphate. Barytes was found to be inactive. Some fluorites showed activity, others did not. F. S.

Radioactive Minerals in the Collection of the Wagner Free Institute of Science. CARL BOYER and EDGAR T. WHERRY (*Trans. Wagner Inst. Sci. Philadelphia*, 1910, **7**, 31).—Plates are given showing the relative activity to the photographic plate of many of the common radioactive minerals. In a table, the activity of sixteen minerals to the electroscope and to the photographic plate respectively are recorded. F. S.

Radioactive Minerals in Common Rocks. JOHN W. WATERS (*Phil. Mag.*, 1910, [vi], 903—904. Compare Abstr., 1909, ii, 848).—Dalbeattie granite yielded as its most radioactive constituent, allanite. Other heavy minerals present were magnetite, sphene, and apatite, which were but feebly radioactive.

In Mourne granite, similarly, the most active constituent was zircon containing small amounts of a titanium mineral, and in this

case the activity was sufficient to produce scintillations on a zinc sulphide screen. It was intended to use these minerals in the determination of the geological age of the specimen by means of the helium ratio, but owing to their size being of the same order as that of the range of the α-ray in minerals (0·04 mm.), results so obtained would not be trustworthy. F. S.

Radioactivity of the Mineral Springs of the Tyrol. II. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1910, **31**, 221—244).—Tables are given of the amounts of radium emanation, expressed in Mache units, in very numerous mineral springs and sources of common drinking water in the Tyrol. The presence of radium in some of the more active waters was proved by boiling out the emanation, and re-testing the water after it had been kept a long time in a tightly closed flask. In another table the radioactivity of numerous stones of the district, and of the sediments from the active springs, is given. The most active water and sediments are those of the Bad Froy at Villnösstal, the former showing an activity of from 30 to 40. The rock in the neighbourhood is described as a graphitic phyllite.
F. S.

Ionisation of Air by the Carbon Monoxide Flame and by Radium Radiation. Mobilities of the Ions Present. MAURICE DE BROGLIE (*Compt. rend.*, 1910, **150**, 1425—1426).—The combustion of dry filtered carbon monoxide gives rise to ions of a totally different order of mobility from those produced by the moist gas.

Direct comparison of the ions produced in air by radium and by a dry carbon monoxide flame showed that the mobility of the positive ions is 20% greater, and of the negative ions 70% greater, in the case of radium. Having regard to the considerable experimental error, and to the presence of some carbon dioxide in the one case, the author draws the conclusion that the ions produced by the combustion of carbon monoxide and by radium have very similar mobilities and are probably identical. R. J. C.

Electrical Conductivity of Alloys and their Temperature-coefficients. III. W. GUERTLER (*Physikal. Zeitsch.*, 1910, **11**, 476—479. Compare Abstr., 1908, ii, 557).—Polemical against Rudolfi (Abstr., 1908, ii, 923). H. M. D.

Ionisation of Salts in Mixtures with no Common Ion. MILES S. SHERRILL (*J. Amer. Chem. Soc.*, 1910, **32**, 741—748).—Determinations have been made of the conductivity of solutions of mixtures of potassium chloride and sodium sulphate, and of sodium chloride and potassium sulphate. The measurements were made at 18°, and at concentrations of $0{\cdot}2N$ and $0{\cdot}1N$. The results show that when the concentrations of the separate ions of the salts in the mixtures are calculated by the principle expressed by the equation: $(A)(B)/A_xB_y = K(\Sigma i)^{2-n}$, where Σi is the total equivalent ion concentration, the sum of the ion concentrations is obtained with an accuracy of about 0·5% at $0{\cdot}2N$, and of about 0·25% at $0{\cdot}1N$. E. G.

Dielectric Cohesion of Neon and its Mixtures. Quantitative Analysis Based on Measurement of Dielectric Cohesion. EDMOND BOUTY (*Compt. rend.*, 1910, **150**, 1380—1383. Compare this vol., ii, 178).—The dielectric cohesion of neon is smaller than that of any other gas. By successive fractionations, the author has reduced the cohesion of neon to 6·1. Extrapolation gives 5·6 as the dielectric cohesion of absolutely pure neon, helium having cohesion 18·3 and hydrogen 205. A series of measurements on mixtures of neon and carbon dioxide (418) and of neon and air (419) shows that the resultant dielectric cohesion is very much higher than that calculated from the law of mixtures when the proportion of diatomic gas is small. The same formula expresses the effect of carbon dioxide and of air on neon when the proportion of neon is at least 97·5%. By means of this formula it is estimated that neon of dielectric cohesion 6·8 contains less than one-twentieth % of impurity, and the purest neon obtained (6·1) less than one-fiftieth % of impurity calculated as air. R. J. C.

Potential of the Thallium Electrode. GILBERT N. LEWIS and CARL L. VON ENDE (*J. Amer. Chem. Soc.*, 1910, **32**, 732—741).—The value of the potential of the thallium electrode in solutions of thallous chloride and nitrate has been determined. It has been found that, contrary to the view of Neumann (Abstr., 1894, ii, 373) and others, the electromotive behaviour of the thallous ion is in no way anomalous. Denham's statement (Proc., 1908, **24**, 76) that, in presence of the thallous ion, thallium forms sub-thallous ions could not be confirmed. Earlier measurements of the thallium potential were vitiated by the oxidation of the electrode and the consequent increase in thallous ion concentration. On taking precautions to avoid such oxidation, it has been found that Nernst's formula holds for the thallium electrode over a large range of concentration with greater accuracy than has been shown to be the case with any other electrode. The assumption of the validity of Nernst's formula and the solubility product rule leads to measurable errors when the concentration is as high as $N/10$, and the direction of these errors can be predicted.

The potential of thallium in saturated solutions of thallous chloride, in $N/10$-potassium chloride, and in N-potassium chloride has been determined. The potential of thallium against the hypothetical normal thallous ion is 0·6170 volt at 25° when the normal calomel electrode is taken as zero. The value 0·602 volt found by Brislee (Abstr., 1909, ii, 463) was obtained at about 17°. The difference between these values may be due to the difference in temperature, but, if so, the thallium electrode must have an exceptionally high temperature-coefficient. E. G.

Cathode Fall [of Potential] in Argon at a Potassium Electrode and its Diminution by the Photoelectric Effect. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1910, **12**, 411—413. Compare Dember, Abstr., 1906, ii, 516).—The author has measured the alteration of the cathode potential fall when a potassium electrode

is illuminated by a mercury vapour quartz lamp. When the discharge tube was filled with argon at a pressure of 5 mm. of mercury and the current passing was such as to give a normal fall of potential, this was found to be reduced from 64 to 38·5 volts when the rays from the lamp where admitted to the electrode through a quartz window. By interposing a glass plate, 2 mm. thick, the fall of potential was reduced from 64 to 47 volts. When the current passing through the tube was increased so as to make the cathode potential fall abnormal, the effect of illuminating the electrode was exactly opposite, the potential difference being increased by 8--10 volts. H. M. D.

Production of Negative Electricity during the Reaction of Gases on Base Metals. FRITZ HABER and GERHARD JUST (*Zeitsch. Electrochem.*, 1910, **16**, 275—279).—An alloy of sodium and potassium is allowed to drop slowly from a tap funnel. The drops fall along the axis of a cylinder of platinum gauze, which is carefully insulated and connected to an electroscope. In an atmosphere of pure dry hydrogen or nitrogen, the potential of the platinum cylinder falls from $22\frac{1}{2}$ to 21 volts in about four minutes, when it is positively charged, or in six and a-half minutes when the charge is negative. This is independent of whether the metal is dropping or not. When a trace of water vapour is admitted, the same fall of potential takes place in seven or eight seconds when the metal is dropping through the positively-charged cylinder, whilst with a negative charge the leak is the same as in dry gas. Hydrogen chloride, iodine vapour, and oxygen give much the same effect in water vapour. Thionyl chloride and carbonyl chloride give much greater effects; with the latter especially, the whole positive charge disappears almost instantaneously, whereas a negative charge is not affected. In every case in which the electrical action occurs, the bright surface of the drops is tarnished. The effect takes place in the dark, but is more marked in the light. It is attributed to the escape of some of the negative electrons in the metal during the chemical change. T. E.

The Electromotive Properties of the Mercury Oxides. ARTHUR JOHN ALLMAND (*Zeitsch. Elektrochem.*, 1910, **16**, 254—263).—The potential difference between mercury and *N*- or 0·1*N*-solutions of sodium or potassium hydroxide containing mercuric oxide in excess is measured at 18°, the potential difference of the *N*-calomel electrode being taken as 0·283 volt. Twelve different samples of mercuric oxide (some yellow and some red) were used. In every case the initial potential difference falls gradually to a practically constant final value. It is shown that the differences are entirely due to differences in the size of the particles. The red and yellow modifications are identical, as both contain prisms and apparently quadratic plates; by prolonged shaking with a solution of potassium chloride, the smaller particles disappear, and the same potential difference is then obtained whether the initial substance is red or yellow. The final values obtained, at 18°, are: *N*-NaOH, +0·115 volt; *N*-KOH, +0·112 volt; *N*/10-NaOH or KOH, +0·168 volt. The electrode is recommended as a standard electrode.

From these results the author calculates that the normal potentials: $Hg_2^{\cdot\cdot} \longrightarrow 2Hg$ and $Hg^{\cdot\cdot} \longrightarrow Hg$ are $+0.775$ and $+0.835$ volt respectively. The solubility product of mercuric oxide at 18° is 4×10^{-26}, and its dissociation pressure is 6×10^{-22} atmosphere.

Mercurous oxide gave no definite potential difference; the values fell very quickly to those obtained with mercuric oxide. T. E.

High Sensibility Selenium Cells. F. C. BROWN (*Physikal. Zeitsch.*, 1910, **11**, 481—482).—The preparation of a form of selenium cell, highly sensitive to light, is described. The selenium was obtained by making a mixture of 10 parts of amorphous selenium and one part of the red, crystalline modification into a thick paste with ether, allowing the ether to evaporate at the ordinary temperature, and then heating the mixture for five hours at 170°. The amorphous selenium was prepared by precipitation of a potassium cyanide solution by means of hydrochloric acid; the crystalline form by exposure of a solution of amorphous selenium in carbon disulphide to the action of sunlight.

The electric conductivity of a selenium cell obtained in this way was found to increase three hundred times on exposure to light at 3°. With rise of temperature, the sensitiveness diminished, and at 39° the ratio of the conductivities was only 80. H. M. D.

New Photoelectric Property of Selenium. F. C. BROWN (*Physikal. Zeitsch.*, 1910, **11**, 482—483. Compare preceding abstract). —A new modification of selenium has been obtained, the electric conductivity of which is about a million times as large as the ordinary photoelectric variety. The method of preparation of this form of selenium is not described. It is, however, unstable, shows a slight diminution of conductivity on exposure to light, and the conductivity increases with rise of temperature. H. M. D.

Fuel Batteries. ITZEK TAITELBAUM (*Zeitsch. Elektrochem.*, 1910, **16**, 286—300).—The Jaques cell was first studied. A layer of powdered quicklime was pressed into the bottom of an iron crucible, and an iron cylinder with a serrated lower edge was embedded in the lime. In this way the crucible is divided into two compartments separated by the quick-lime diaphragm. The whole is filled with fused sodium hydroxide, and a carbon electrode placed in the inner compartment. The crucible itself forms the positive electrode, and sodium manganate is dissolved in the outer compartment to serve as an oxygen carrier. The carbon electrode alone gives a very small current, but when fuels, such as sucrose, charcoal, coal or tallow, or gases, such as carbon monoxide, hydrogen or coal gas, are introduced into the inner compartment, considerably larger currents are obtained. The combustion of 0·1 gram of sugar in the cell, for example, yielded 1346 coulombs, instead of 1351 coulombs calculated for quadrivalent carbon. Other substances gave current efficiencies varying from 100% for charcoal to 24% with ordinary coal. The *E.M.F.* of the cell (at 370—390°) varies from 0·75 volt (sawdust) to 0·54 volt (carbon tube) on open circuit, but this falls when a current is taken from the cell; for example, with

0·15 ampere the *E.M.F.* is 0·44 volt with sawdust, and less than 0·1 volt with the carbon tube: the other substances tried gave intermediate values.

A cell was next investigated in which strong sulphuric acid was the electrolyte. The potential difference between platinium and sulphuric acid containing a reducing agent was first measured by combining this electrode with the mercurous sulphate–*N*-sulphuric acid electrode. The same fuels as before were tried at temperatures between 50° and 300°; they give curves running parallel to, and below, that given by sulphur dioxide. The potential of the electrode is due to the presence of sulphur dioxide, formed by the action of the fuel on the sulphuric acid. The main difficulty with the oxygen electrode was to find a substance which would absorb atmospheric oxygen sufficiently rapidly to depolarise the electrode. Ferrous and mercurous sulphates are unsatisfactory. A mixture of vanadyl sulphate and vanadic acid or of thallous and thallic sulphates dissolved in strong sulphuric acid gives good results at temperatures above 200°. At 250° the potential of platinium in either solution in equilibrium with air is 1·35 volts (referred to the normal hydrogen electrode). The combination of the vanadium electrode with the fuel electrode gives an *E.M.F.* which varies between 0·3 and 0·6 volt on open circuit at 250° according to the nature of the fuel used; substances which reduce sulphuric acid rapidly, such as partly carbonised sugar and acetylene, give the highest values and the smallest degree of polarisation when current is taken from the cell. The fuel electrode may be made of carbon, but the oxygen electrode must be of platinum or gold. T. E.

Fuel Batteries. EMIL BAUR (*Zeitsch. Elektrochem.*, 1910, **16**, 300—302).—From the determinations of the dissociation of sulphuric acid and sulphur trioxide made by Bodenstein and Katayama (Abstr., 1909, ii, 468) and a measurement of the vapour pressure of 96% sulphuric acid at 250°, the *E.M.F.* of the combination SO_2 | sulphuric acid | O_2 is calculated to be 0·37 volt at 250°. The higher values (0·5 to 0·6 volt) found by Taitelbaum (preceding abstract) are attributed to the nascent condition of the sulphur dioxide. The *E.M.F.* which should be produced by the reversible combustion of carbon to carbon dioxide is about 1 volt; hence Taitelbaum's cell yields some 50 or 60% of the free energy of the carbon. T. E.

Silver–Nickel Thermo-element. GEORG VON HEVESY and E. WOLFF (*Physikal. Zeitsch.*, 1910, 11, 473—476).—An investigation of the behaviour of the silver–nickel thermo-element between −80° and +920° has shown that it is very suitable for the measurement of temperatures between these limits. The curve showing the connexion between the thermo-electric force and the temperature exhibits neither a neutral nor an inversion point; it cannot be represented by an equation of the second order. The temperature-coefficient of the thermo-electric force has a maximum value between 180° and 220°, and a minimum value at about 370°. Above 370° the temperature-coefficient increases with the temperature up to about 780°, and then remains constant. The minimum value of the temperature-coefficient at 370° is connected with a change in the nickel at this temperature.

The readings of the thermo-element are reproducible with considerable precision. In contact with air at 600° to 700°, the nickel becomes brittle in consequence of the action of oxygen on the metal, and higher values for the thermo-electric force are obtained. H. M. D.

The Thermoelectricity of Alloys. I. ERNST RUDOLFI (*Zeitsch. anorg. Chem.*, 1910, **67**, 65—96).—The thermoelectric behaviour of a number of simple binary alloys, the constitution of which is known, has been examined. The alloys, with the exception of those containing silver and gold, were melted in glass tubes in an atmosphere of hydrogen, and drawn into glass tubes 1·5 mm. in diameter, coated internally, if necessary, with lamp-black. Gold and silver alloys were melted in porcelain crucibles in nitrogen, drawn into porcelain tubes, and afterwards drawn into wire. The thermo-electromotive force of the wires or rods was then measured against copper and against nickel, one junction being in ice and the other in a vessel of paraffin, heated by an outer paraffin-bath. After heating to 170—180°, readings were taken as the temperature fell, a compensation method being used.

The results are compared with previous determinations of the hardness and electrical conductivity (compare Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932). Alloys in which the two components crystallise in the pure state, without forming solid solutions, have a thermo-electric power proportional to the concentration (tin–cadmium, tin–zinc). If there is a slight formation of solid solutions, the line is broken at the limit of saturation of that solution (zinc–cadmium, lead–tin, bismuth–cadmium, lead–antimony). If the two metals form a continuous series of solid solutions, the curve has the U-shape of the conductivity curve (gold–silver, gold–copper, copper–nickel, platinum–palladium). The curves therefore have the same form as those of electrical conductivity (compare Haken, this vol., ii, 387). Solid solutions are the most suitable for the construction of thermopiles.

C. H. D.

Electric Vacuum Furnace. OTTO RUFF (*Ber.*, 1910, **43**, 1564—1574).—An electric furnace is described which may be used either as a resistance or an arc furnace. It is so arranged that it can be filled with a gas other than air, and it may be worked at pressures varying from 3 mm. to one atmosphere. The electrodes are placed vertically, and when used as a resistance furnace the resistance consists of a carbon tube inside which a small carbon crucible is supported. Opposite the crucible there is a slit in the tube, and the wall of the furnace also contains a quartz window, so that the temperature may be taken by means of a Wanner pyrometer. Temperatures of 1000—2700° can readily be obtained in a few minutes, and the furnace will withstand temperatures of 2000—2200° for several hours. The power required varies from 200 amperes at 15 volts to 700 amperes at 41 volts. When the vacuum is satisfactory, the carbonising effect of the furnace atmosphere on the substance being heated is inappreciable.

Vanadium (96—97%) was readily obtained by the reduction

of vanadium trioxide with carbon. The following melting points were determined: platinum, 1745—1755°; molybdenum, 2110°; iridium, 2210—2225°; kaolin, 1912—1915°; tungsten (99·2%), 2575°. Titanium containing 5% of carbon could not be melted completely at 2700°.

The oxides of aluminium, magnesium, and calcium were found to be more volatile and fusible than hitherto supposed. At low pressures (5 mm.), and with small quantities of substance, they were completely volatile below the melting point. In nitrogen at atmospheric pressure, aluminium oxide had m. p. 2065°; the melting point of calcium oxide was in the neighbourhood of 2000°, but could not be exactly determined; magnesium oxide vaporised rapidly at 2100°, but the m. p. is certainly much lower than 2500° (compare Arndt, *Chem. Zeit.*, 1906, **30**, 211). The furnace was so adapted that the electrical conductivity of these oxides could be measured, and it was found that there is a big increase in the conductivity when fusion takes place.

Silicon tetrafluoride is not acted on by carbon, even at the highest temperatures used. T. S. P.

Process of Rapidly Forming Lead-Accumulator Plates by means of Phosphoric Acid and Phosphates. FRANZ FISCHER (*Zeitsch. Elektrochem.*, 1910, **16**, 355—357).—The lead plate to be formed is placed between two others (1 cm. distant) in a 10% solution of disodium hydrogen phosphate at 80°. The applied *E.M.F.* is 2·2 volts, and it must never exceed 2·6 volts. After twenty-four to thirty-six hours, an adherent layer of lead monoxide is produced on the anode, which is readily reduced to lead, but is very slowly oxidised to peroxide. Lead phosphate is probably the initial product, and this is decomposed by the sodium hydroxide formed at the cathode; a diminution of volume occurs in the change, and the layer of oxide is therefore porous. The volume diminishes further when the oxide is reduced to lead, but increases when it is oxidised to peroxide, which explains the difference in the rates of these changes, the increase of volume filling up the pores and so confining the action to the surface.

The formation of the plate is therefore completed by reducing it in sulphuric acid of D 1·18 with 0·01 ampere per sq. cm., washing it free from phosphoric acid, and then charging it (as anode) in sulphuric acid of D 1·09 at the same current density until oxygen is evolved freely. The reduction requires the same time as the formation, and the oxidation twice as long. The whole operation occupies four or five days.

T. E.

Electrolysis of Alkali Bromides and Retardation of the Anodic Separation of the Halogens. FRITZ FOERSTER and J. YAMASAKI (*Zeitsch. Elektrochem.*, 1910, **16**, 321—355).—A very extensive and accurate series of experiments is recorded on the electrolysis of sodium bromide. The influence of alkalis, concentration, temperature, rate of stirring, current density, and platinising the anode are studied in detail. The results are in complete agreement with the theory of the process given by Kretzschmar (Abstr., 1904, ii, 814).

At platinum anodes, bromine is liberated at the reversible bromine potential only when the anode is quite free from oxygen. When the platinum contains oxygen, a higher potential is required. The excess potential required is especially large at smooth platinum surfaces and in alkaline solutions. Similar effects have been observed with chlorine and oxygen itself, and they are doubtless due, as Luther and Brislee suppose (Abstr., 1903, ii, 708), to the formation of compounds of platinum and oxygen on the surface of the anode.

T. E.

Electrolytic Formation of Films of Zinc on the Surface of Liquids. HERBERT FREUNDLICH and W. NOVIKOW (*Zeitsch. Elektrochem*, 1910, **16**, 394—400).—The formation of floating films of zinc studied by Mylius and Fromm (Abstr., 1894, ii, 267) is again investigated. The formation of the film only occurs in an atmosphere containing oxygen (at least 1% mixed with nitrogen, carbon dioxide, or hydrogen), and the surface of the zinc sulphate solution must be covered by a film of some liquid which does not mix with it. Oxidation of the zinc is of secondary importance, but the formation of the film depends on the primary separation of zinc sponge (amorphous zinc) which is favoured by oxygen. The nature of the zinc sponge is uncertain; it always contains oxide, which remains undissolved when the current is reversed. The presence of small quantities of ammonium salts, salts of amines, tartaric acid, citric acid, and potassium cyanide in the 50% zinc sulphate solution prevents the formation of the film. The ammonium salts are the most active: 0·0005 mol. of ammonium sulphate to 1 mol. of zinc sulphate is sufficient. The action is apparently due to an acceleration of the change of amorphous into crystalline zinc. A thin layer of almost any liquid which does not mix with the zinc sulphate solution or of any solid (so long as it remains pasty) brings about the film formation. The thickness of layer necessary is found to be from 0·5 to $2\mu\mu$. T. E.

Theory of Electrolytic Ions. IV. Coincidence of the Diameter of Atoms and of Ions not Related to the Solvent. RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1910, **73**, 252—255).—Compare Abstr., 1909, ii, 541).—The diameters of a number of univalent elementary ions have been calculated from the ionic mobilities by Einstein's formula, which at 18° reduces to $\mu_{18} = 1/\rho . 7{\cdot}562 \times 10^{-7}$, where μ_{18} is the ionic mobility at 18°, expressed in the usual units, and ρ is the radius of the ion. The results are compared with the diameters of the respective atoms, calculated by Reinganum's formula (compare Rappenecker, this vol., ii, 590), $\sigma = 2\rho = 0{\cdot}882 . 10^{-8}\sqrt[3]{m/d}$ cms., in which σ is the molecular diameter, m the molecular weight, and d the density of the substance in the liquid state at its boiling point, and it is shown that the diameter of the ions is of the same order as that of the free atoms ($2{\cdot}6 \times 10^{-8}$ cm.), with the exception of lithium, for which the ionic diameter is more than double that of the atom. It follows that the ions in general cannot be highly hydrated; they may, however, be associated with three or four molecules of water. The lithium ion is hydrated to a considerable extent.

This does not apply to ions related to the solvent, the diameters of the hydrogen and oxygen atoms being three to four times those of the ions, as calculated from the ionic velocities. G. S.

The Relation between the Formation of Nitric Oxide and the Electrical and Thermal Properties of Short Direct Current Arcs with a Cooled Anode. WILHELM HOLWECH (*Zeitsch. Elektrochem.*, 1910, **16**, 369—390).—The combustion of atmospheric nitrogen in a short arc formed between a water-cooled silver anode and a heated cathode was studied. The cathode was a strip of iridium foil, coated with lime, and heated by an independent current to a temperature not far short of its melting point. The arcs studied were from 0·8 to 4 mm. long; the current was varied from 0·07 to 0·2 ampere, and the voltage required lay between 90 and 300 volts.

The highest concentrations of nitric oxide were obtained with stationary gas, the shortest arc (1 mm.), and 500—600 mm. pressure; in these circumstances over 9% of nitric oxide was obtained, using air. The yield (of nitric acid) was 70 to 80 grams per kilowatt-hour, and this was almost independent of the length of the arc.

A careful study of the electrical properties of the arc showed that the anode and cathode falls of potential take place just at the surface of the electrodes; the distance through which they extend was too small to be measured; the fall of potential along the arc was quite constant. The falls of potential at the electrodes therefore have no influence on the formation of nitric oxide; they do not even effect the temperature of the electrodes, the one being cooled and the other heated independently of the current in the arc. The formation of nitric oxide is therefore entirely controlled by the fall of potential along the arc and the current flowing. The fall of potential varied from 100 to 200 volts per cm., whilst in the long arcs used in manufacturing practice it is under 10 volts per cm.

The temperature of the short arcs is lowest near the cooled anode, and it increases with the pressure of the air. A very fine platinum wire placed in the arc quite close to the anode did not melt when the pressure was 1 atmosphere; at 100 mm. pressure it could be moved 3 or 4 mm. away from the anode before it melted. The very fine iridium point which was plunged into the arc in order to measure the fall of potential along it never showed the slightest indication of fusion, and the temperature of the iridium cathode which was at the hottest end of the arc could not exceed the melting point of iridium without stopping the experiment. It is therefore regarded as certain that the temperature of the arc nowhere exceeded 3000° absolute, at which temperature the purely thermal equilibrium between oxygen, nitrogen, and nitric oxide corresponds with about 4% of nitric oxide in the mixture. The formation of nitric oxide in these experiments is therefore due to collisions of ions, whereas in the low tension arcs employed in practice it is probably a thermal phenomenon. T. E.

Magnetisation of Liquid and Solid Oxygen. H. KAMERLINGH ONNES and ALBERT PERRIER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **12**, 799—835).—Measurements have been made of the magnetic

susceptibility of liquid and solid oxygen. Between $-183°$ and $-208°$ the specific susceptibility of liquid oxygen is inversely proportional to the absolute temperature, and can be represented by the equation: $\chi = 0·002284/\sqrt{T}$. The variation of the susceptibility of solid oxygen with temperature is exactly similar, and can be represented by $\chi = 0·001690/\sqrt{T}$, which holds between $-259°$ and the melting point of oxygen. The two equations indicate that the susceptibility of liquid oxygen at its freezing point is 1·3 times as great as that of the solid form.

It is probable that the observed variation of the magnetic susceptibility with the temperature gradually changes its form as the temperature rises, and that at higher temperatures the variation is in agreement with Curie's law, according to which the susceptibility is inversely as the absolute temperature. H. M. D.

The Magnetic Properties of the Modifications of Iron. SIEGFRIED HILPERT (*Zeitsch. Elektrochem.*, 1910, **16**, 390—394).—A theoretical discussion. Between 700° and 760° iron becomes practically non-magnetic, and its specific heat exhibits anomalies. These phenomena are usually ascribed to the formation of β-iron. The author thinks that the anomalous specific heat may be due to the breaking up of the polar arrangement of the magnetic molecules by their more energetic vibration at high temperatures. This would absorb energy, and so explain both the disappearance of the magnetism and the anomalous specific heat without the assumption of a new modification of iron.

γ-Iron is also supposed to be magnetic at low temperatures, and to lose its magnetism at high temperatures in the same way as α-iron. This explains why steels containing martensite are readily magnetised.

T. E.

Influence of the Magnetic Field on the Passive State of Iron. HORACE G. BYERS and MARC DARRIN (*J. Amer. Chem. Soc.*, 1910, **32**, 750—756).—It has been shown by Byers (Abstr., 1908, ii, 1026) that when iron is used as an anode in various electrolytes, it can be rendered passive by a definite current density. Nichols (Abstr., 1886, 668) has found that the passive state of iron in nitric acid can be destroyed by placing the metal in a strong magnetic field. It was therefore considered of interest to ascertain whether the passive state of iron used as an anode would be similarly affected by the magnetic field.

As a result of experiments, it was found that the passive state could not be destroyed by any magnetic field producible with the apparatus available. It is shown that in solutions of nitric, sulphuric, and phosphoric acids, and also of nitrates and sulphates, the transition point of passive to active iron is a function of current density, and that the transition is retarded by the magnetic field. It is suggested that passivity is the result of an altered state of the metal itself, and that the altered state may be analogous to that of a number of magnets, the negative poles of which are all presented to the electrolyte, the orientation being produced by the various agents which cause the passive state. E. G.

Magnetic Analysis of Certain Chromophoric Groups. PAUL PASCAL (*Compt. rend.*, 1910, **150**, 1167—1169. Compare this vol., ii, 100).—The molecular susceptibility of an organic substance is composed of two factors ($A + B$). A is the sum of the separate susceptibilities of the atoms, and B consists of a series of corrections for structural peculiarities, such as double linkings, etc. The quantities B comprise a considerable part of the whole susceptibility, so that tautomeric changes of structure may give rise to very appreciable differences in susceptibility.

Aminoazobenzene, aminoazotoluene, and chrysoidine have susceptibilities almost identical with those calculated for the azo-structure. Hydroxyazobenzene, methoxyazobenzene, and benzeneazo-β-naphthol are mixtures of the azo- and quinone forms.

p-Azoanisole and *p*-azophenetole exist in two forms. The colourless form has a susceptibility corresponding with the azo-formula, whilst the red form, which is obtained on heating, has the much lower susceptibility of the quinonoid structure. Crystals of *p*-azoanisole of all gradations of colour, from colourless to red, can be obtained, giving corresponding intermediate values of the susceptibility.

Aurine appears to have the quinonoid structure, whereas magenta and other amino-derivatives of triphenylmethane are enolic.

The colourless form of the silver salt of 2 : 4 : 6-tribromophenol is a normal phenoxide, whereas the red form is quinonoid. R. J. C.

Relation between the Specific Heats of Solid Substances and Temperature. ALFRED MAGNUS and F. A. LINDEMANN (*Zeitsch. Elektrochem.*, 1910, **16**, 269—272).—From Planck's theory of radiation, Einstein (*Ann. Physik*, 1907, **22**, 180) has obtained an expression for the atomic heat of an element at constant volume: $C = 3Rn\{e^A A^2/(e^A - 1)^2\}$, where $A = \beta\nu/T$, n is the number of atoms in a molecule, β a constant ($4{\cdot}86 \times 10^{-11}$), and ν is the frequency of vibration of the atoms. The authors find that by adding an empirical member, $aT^{3/2}$, to the expression, the specific heats at constant pressure, as they are always measured, may be represented with considerable accuracy. For the metals, n can be taken as unity; for the metalloids this gives a considerably less satisfactory agreement. The frequencies of the elements are in the same order as the values of $\sqrt{S/VA}$ (S = melting point, V = atomic volume, A = atomic weight). The values calculated are:

	$\nu \times 10^{-12}$.	$3\sqrt{S/VA}$.	$a \times 10^5$.
Bi	small	1·1	5·1
Pb	1·2	1·2	7·8
Sn	2·7	1·5	10·5
Cd	2·7	1·9	6·8
Sb	3·1	1·9	4 2
Pt	3·1	3·2	6·3
Ag	3·3	3·2	4·8
Zn	3·7	3·2	6·1
Mg	5·1	4·9	6·5
Cu	5·3	5·2	3·8
Al	6·8	5·6	5·2
Cr	7·2	6·4	5·6
I	2·7	1·0	15·5
S	5·5	2·6	—
Si	10·7	6·7	—
Graphite	22·6	>21·0	—
Diamond	27·3	>26·0	—

T. E.

Calculation of Electromotive Forces from Thermal Measurements. ALFRED MAGNUS (*Zeitsch. Elektrochem.*, 1910, **16**, 273—275).—The free energy of the reaction $Pb + 2AgCl = PbCl_2 + 2Ag$ has been measured accurately by Broenstedt, and compared with Nernst's theorem by Halla (Abstr., 1908, ii, 755). The specific heats of the reacting substances are now more accurately known; the measurements are well represented by the formula obtained by Magnus and Lindemann (preceding abstract), using the following constants:

	$\beta\gamma$.	$a \times 10^5$
Lead	58	7·8
Silver chloride	168	22·0
Lead ,,	172	18 0
Silver	162	4·8

The only marked difference is in the case of Dewar's determination of the specific heat of lead between the boiling points of air and hydrogen. From the specific heats, the relation between the heat of the reaction and the temperature is obtained, and this makes it possible to calculate the free energy from the equation: $A = -T\int Q/T_2 dT$, which follows from Nernst's theorem. The largest difference between the free energy calculated and that found is 0·2%. T. E.

Energy Changes in Binary Systems. I. Confirmation of the Existence of the Compound Phenol-aniline in the Liquid State. ROBERT KREMANN (*Monatsh.*, 1910, **31**, 203—209. Compare Kremann and Ehrlich, Abstr., 1907, ii, 747).—The specific heats of the system phenol-aniline have been determined at different temperatures above the m. p. The method adopted was to raise 20 grams of an equimolecular mixture of aniline and phenol, sealed in a glass vessel, to the required temperature, and then to transfer quickly to a water calorimeter. Details of the corrections made are given. The sp. heat for the interval 99·0—74·9° is 0·376, which is the true specific heat for the equimolecular mixture of aniline and phenol; the value obtained for the interval 90—33·7° is 0·407, and the difference between the two values, namely, 0·031 × 65·7 cal. = 2 cal., is the value for the heat of formation of the compound between the temperatures 33·7° and 99°.

The heats of admixture of equivalent quantities of aniline and phenol at different temperature intervals have been determined, and as expected, the observed heats diminished with rise in temperature. These observed heats are the actual heats of admixture plus the heat of formation of the additive compound, if such is formed. Since, however, with increase in temperature there is a tendency for the additive compound to dissociate, it follows that the amount of additive compound present diminishes with rise in temperature, and the observed heats of admixture must also diminish. The value found is about 1 calorie for an increase of 35·7°. J. J. S.

Cryoscopic Determinations at Low Temperatures (−40° to −117°). ERNST BECKMANN and PERCY WAENTIG [with M. NIESCHER] (*Zeitsch. anorg. Chem.*, 1910, **67**, 17—61).—Pentane thermometers are

not satisfactory for work at low temperatures, on account of the viscosity of the pentane, the deposition of solid at very low temperatures, and the varying solubility of the gas used for filling. The platinum resistance thermometer, having the platinum wire wound on quartz or Jena glass, gives perfectly satisfactory results. The pattern used has a resistance of 25·3 ohms at 0°. One millimetre on the scale of the Wheatstone bridge, with the arrangement adopted, corresponds with 0·0017°.

The freezing apparatus has been already described (Beckmann, Junker, and Klopfer, Abstr., 1909, ii, 137). A bath of light petroleum, cooled by a spiral containing liquid air, is used.

The following cryoscopic constants have been obtained: carbon tetrachloride 298, pyridine 49·7, chloroform 46·8, ethyl ether 17·9, hydrogen iodide 202 6, hydrogen bromide 94·1, hydrogen chloride 49·8, hydrogen sulphide 38·3. Toluene and cymene are suitable substances for determining the constants.

Chloroform and carbon tetrachloride resemble benzene in their very small dissociating power. Alcohols, dissolved in them, give high values for the molecular weight. The halogen hydrides have also only a small dissociating power, and compounds containing hydroxyl show association when dissolved in them. The conductivity of the solvent increases from hydrogen iodide to hydrogen bromide. In the solutions, a higher conductivity often accompanies a higher molecular weight (compare Steele, McIntosh, and Archibald, Abstr., 1905, ii, 222). Benzophenone exhibits association and conductivity, increasing with the concentration, in hydrogen iodide, becoming successively less in hydrogen bromide and chloride. Acetone is associated in hydrogen iodide, corresponding with the compound, $2C_6H_8O,HI$, found by McIntosh and Archibald, (Trans., 1904, **85**, 919). Iodine is similarly associated in pyridine. Ethyl acetoacetate is not associated in chloroform.

Water does not dissolve in liquid hydrogen chloride, but dry ammonia at once forms ammonium chloride. Liquid hydrogen sulphide, which blackens white lead, but is without action on silver, has little dissociating power. Compounds containing hydroxyl are slightly associated in it. Benzophenone appears to be dissociated in dilute solution in hydrogen sulphide, but no electrical conductivity is detected.

The latent heats of fusion of the solvents used are calculated, and the desirability of determinations of the dielectric constants at low temperatures is pointed out. The methods of preparation of the liquefied hydrogen halides and sulphide are described. C. H. D.

Properties of Iodine as a Cryoscopic Solvent. F. OLIVARI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 488—489).—The author corrects certain of the results given in his previous paper (this vol., ii, 18).

Lead iodide cannot be employed as a solute for determining the molecular freezing-point depression of iodine, as it is insoluble in this solvent. For oxygenated organic compounds, as well as for the hydrocarbons and their halogen derivatives, the molecular weights in iodine solution are normal at very great dilutions. With potassium

iodide, the molecular weight appears to be approximately normal for very dilute solutions, increase of the concentration being accompanied first by increase, and later by decrease of the molecular weight.

T. H. P.

Vaporisation. IV. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1910, **73**, 173—191. Compare Abstr., 1909, ii, 21).—By a combination of Mendeléeff's expansion modulus for liquids with some well-known rules referring to the relationships of the volumes of liquids and their saturated vapours, it is shown (1) that the temperature-coefficient of the density and the thermal expansion-coefficient have opposite signs; (2) the magnitude of both is the smaller the higher the critical temperature; (3) up to $T=0{\cdot}7T_k$, the temperature-coefficient of the density remains constant, whilst the expansion-coefficient increases with the temperature.

For low temperatures the ratio of the density, D_l, of the liquid at the temperature, T, to the critical density can be calculated by the simple expression: $D_l/D_k=4(1-T/2T_k)=2(2-\theta)$, where $\theta=T/T_k$, but at higher temperatures the more complicated expression: $D_l/D_k=2-\theta-2\sqrt[3]{1-\theta}-x\sqrt[3]{(1-\theta)^2}$ is used, and for the ratio of the density of the vapour D_v to the critical density the corresponding expression: $D_v/D_k=2-\theta-2\sqrt[3]{1-\theta}+x\sqrt[3]{(1-\theta)^2}$. The expressions are tested by comparing the calculated and observed data for fluorobenzene and for ammonia, and the agreement, especially for the two latter formulæ, is excellent; x is a constant, and for fluorobenzene is 0·194, for ammonia, 0·1. A slight modification of the first formula, $D_l/D_k=2+1{\cdot}87(1-\theta)$, is shown to give very good results up to $T=0{\cdot}65T_k$.

From the above equations, formulæ are derived which admit of the calculation of the volumes of the liquid at different temperatures.

G. S.

Vapour Pressures of Binary Mixtures. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1910, **72**, 723—751).—The author adversely criticises the recent work of Dolezalek (Abstr., 1909, ii, 22; this vol., ii, 184), who has applied the laws of dilute solutions to certain binary systems, and also the mathematical treatment of the partial pressures of binary mixtures by Story (compare this vol., ii, 184) and others, and points out that a satisfactory theoretical treatment is only possible on the lines laid down by van der Waals and by himself. The most important point is that the attraction factor a must be taken into account. All the possible types of vapour pressure curves for binary mixtures are discussed mathematically. G. S.

Fractionating Arrangement. ARNOLD HAHN (*Ber.*, 1910, **43**, 1725—1727).—The ordinary fractionating column possesses the disadvantage that the separate fractions all pass through the same side-tube. The arrangement described consists of a bulb tube with a ground-glass neck, into which fits a ground-glass stopper carrying the thermometer. Into the neck of the bulb tube are fused three side-tubes, each of which is connected with a receiver. The glass stopper

contains one hole, which can be placed opposite to each of the side-tubes in succession, the other two being meanwhile closed.

When used for distillations under diminished pressure, the three receivers are connected to a 4-way tube leading to the pump, but although all the receivers are evacuated at the same time, only one is in direct connexion with the distilling flask at any particular moment; consequently, there is no contamination of one fraction by vapours derived from other fractions. T. S. P.

Calibration and Manipulation of the Calorimetric Bomb. WALTER A. ROTH (*Annalen*, 1910, **373**, 249—266).—A less elaborate method than Fischer and Wrede's electrical process of calibrating a calorimetric bomb is described in detail, the necessary corrections being carefully explained. The bomb is Hugershoff's Precision Model; the calorimetric thermometer is a Beckmann thermometer, by means of which 1/2000° can be estimated. The results are accurate to within 0·1%. The trustworthiness of the method is proved by determining the total water equivalent of the calorimetric apparatus by exploding sucrose, benzoic acid, and naphthalene; taking the heats of combustion per gram of these substances as 3952·0 cal., 6325·4 cal., and 9640·5 cal. respectively, the water equivalent is found to be $2623·3 \pm 0·6$ cal., $2623·4 \pm 0·8$ cal., and $2622·5 \pm 0·7$ cal. The calibration is controlled by a fourth process, in which a known quantity of heat is generated electrically within the bomb; the water equivalent in this case is $2623·1 \pm 1·0$ cal.

C. S.

Heat of Formation of Cæsium Peroxide. ROBERT DE FORCRAND (*Compt. rend.*, 1910, **150**, 1399—1402. Compare Abstr., 1906, ii, 445).—The heat of dissolution of 1 gram-molecule of cæsium peroxide, Cs_2O_4, in an equivalent of 2% sulphuric acid is 33·02 Cal., from which the following thermal equations are deduced:

$$Cs_2 \text{ (sol.)} + 2O_2 \text{ (gas)} = Cs_2O_4 \text{ (sol.)} + 141·46 \text{ Cal.}$$
$$Cs_2O \text{ (sol.)} + 3O \text{ (gas)} = Cs_2O_4 \text{ (sol.)} + 58·76 \text{ Cal.}$$

The heat of complete oxidation of cæsium (+141·46 Cal.) is very near that of complete oxidation of lithium (Li_2O, +143·32 Cal.), and the oxidation of strontium to monoxide (SrO, +138·64 Cal.), but is less than the heat of complete oxidation of strontium (SrO_2, +151·71 Cal.). The first oxygen atom combining with Cs_2 gives +82·70 Cal., whereas the average for the next three atoms is +19·59 Cal. each. In the case of the sodium oxides, Na_2O and Na_2O_2 are stable, whereas Na_2O_3 and Na_2O_4 are completely dissociated under ordinary conditions. It is argued by analogy that the 58·76 Cal. evolved in passing from Cs_2O to Cs_2O_2 should not be distributed among the successive oxygen atoms equally, but in a decreasing ratio. Supposing that the temperature of dissociation of Cs_2O_4 to $Cs_2O_3 + O$ is about 550°, the heat of addition of the last oxygen atom would be about 12·5 Cal. The author suggests that the addition of oxygen atoms to Cs_2O liberates 28·26, 18·0, 12·5 Cal. successively.

The heat of formation of Cs_2O_4 from Cs_2O is practically as great as the heat of hydration of Cs_2O to $2CsOH$ (60·01 Cal.). At 300°

to 400°, the order of these two values is reversed, so that on heating cæsium hydroxide in oxygen, cæsium peroxide would be exothermally produced with evolution of steam. Owing to the silver boats being attacked, pure cæsium peroxide cannot be obtained in this way.

R. J. C.

Heat of Formation of the Oxides of Molybdenum, Selenium, and Tellurium; Heat of Combination of Acidic Oxides with Sodium Oxide. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1910, [iv], **29**, 488—496. Compare Abstr., 1909, ii, 865).—The heats of formation of the oxides and sodium salts have been calculated from the thermal data obtained by oxidising the elements or lower oxides by means of sodium peroxide. The following results are given: $Mo + 3O = MoO_3$, + 181·5 Cal.; $Na_2O + MoO_3 = Na_2MoO_4$, + 81·9 Cal.; $Mo + 2O = MoO_2$, + 142·8 Cal.; $Se + 3O = SeO_3$, + 48·8 Cal.; $Na_2O + SeO_3 = Na_2SeO_4$, + 105·3 Cal.; $Te + 3O = TeO_3$, + 83·6 Cal.; $Na_2O + TeO_3 = Na_2TeO_4$, + 124·3 Cal.; $Te + O_2 = TeO_2$, + 87·1 Cal. According to the heats of formation of the two oxides of tellurium, the conversion of the dioxide into the trioxide is an endothermic reaction.

H. M. D.

Heat of Combination of Hydrogen Bromide with some Ethylenic Compounds. WLADIMIR LUGININ and GEORGES DUPONT (*Compt. rend.*, 1910, **150**, 1346—1348. Compare Berthelot, Abstr., 1876, i, 870).—Berthelot's determinations of the amount of heat developed on the addition of halogen acids to unsaturated compounds are untrustworthy, owing to the small amount of the substances entering into combination in aqueous solution. More accurate results have been obtained by utilising xylene as the solvent; the heat of dissolution (Q) of one gram-molecule of hydrogen bromide in this substance is given by $Q = 6{\cdot}344 - 51{,}000x + 188{,}000x^2$, where x is the number of gram-molecules of acid in 100 grams of solution. The following values have been obtained for the addition of one gram-molecule of gaseous hydrogen bromide to one gram-molecule of the substance dissolved in xylene. Styrene, 16,653 cal.; octylene, 16,481 cal.; amylene, 17,614 cal.; β-methyl-Δ^{β}-pentylene, 19,008 cal.; *cyclo*hexene, 16,292 cal.; pulegone, 16,910 cal. As the compounds examined and their additive products are liquid, the above numbers are practically identical with the heats of formation of the halogen derivatives.

W. O. W.

Thermochemical Investigations. I. Relation between the Constitution and the Heat of Combustion of Unsaturated Compounds. KARL AUWERS and WALTER A. ROTH (*Annalen*, 1910, **373**, 239—248).—Very little is known regarding the relations between the constitutions of organic compounds and their heats of combustion. The more labile of two isomeric compounds has the greater heat of combustion, but even in unusually favourable cases the difference does not exceed 2%. Hence, any thermochemical method of investigation must be accurate to within 0·1—0·2%. Such accuracy has been attained by several investigators by means of the calorimetric

bomb, but unfortunately their results have not been hitherto certainly comparable. Fischer and Wrede (Abstr., 1909, ii, 155), however, have described a method whereby calorimetric bombs may be calibrated with an accuracy of 0·05%, so that it should now be possible to make the results obtained by different workers strictly comparable.

The authors commence their researches with an investigation of the heats of combustion of unsaturated compounds, particularly of those containing conjugate linkings. Stohmann and Langbein already have shown that the heats of combustion of propenyl compounds are about 0·5 to 0·8% greater than those of the less labile isomeric allyl compounds. Also, Thiele states that the system $C{:}C{\cdot}C{:}C{\cdot}CH_2$ is more saturated than the system $C{:}C{\cdot}CH_2{\cdot}C{:}C$, and therefore has a smaller heat of combustion. Further, it is known that the heats of combustion of $\alpha\beta$-unsaturated acids are smaller than those of $\beta\gamma$-unsaturated acids. Hence it seems that the nearer a pair of doubly-linked atoms are together, the smaller the heat of combustion. This statement is supported by references to the heats of combustion of hexoic, hydrosorbic, and sorbic acids, of diphenyl, diphenylmethane, and dibenzyl, and of *m*-toluic and phenylacetic acids.

The authors call attention to the lack of knowledge of the heats of fusion of organic substances, and utter a needful warning in pointing out that for the heats of fusion of solids there is no generalisation analogous to Trouton's rule for the molecular heats of volatilisation of liquids. C. S.

Heats of Combustion of Terpenes and Styrenes. KARL AUWERS, WALTER A. ROTH, and FRITZ EISENLOHR (*Annalen*, 1910, **373**, 267—290).—The molecular heats of combustion, expressed in Calories, of the following terpenes have been measured: *d*-limonene, 1466; dipentene, 1462; sylvestrene, 1464; α-phellandrene, 1434; carvenene, 1424; α-terpinene, 1428; *d*-α-pinene, 1469; *l*-α-pinene, 1467; camphene (liquid), 1471; sabinene, 1475.

Since empirical expressions for the determination of "calculated values" of heats of combustion are not trustworthy, the following method is adopted to obtain values whereby the thermal and the optical (refractivity and dispersivity) behaviours may be compared. The mean value, 1464, of the molecular heats of combustion of limonene, dipentene, and sylvestrene, three hydrocarbons containing two double (not conjugated) linkings, is taken as the "normal value" of the molecular heat of combustion of hydrocarbons of the terpene group. The molecular "depression," that is, the difference, expressed as a percentage, between the normal value and the actual value of the molecular heat of combustion of a terpene, is compared with the exaltation of the molecular refractivity and dispersivity, calculated from the formula $C_{10}H_{16}|^{=}_{2}$. In this way, it is at once obvious that terpenes containing a conjugate linking have smaller heats of combustion (about 2%) than those which do not contain such a system, and also that the thermal "depressions" are of the same order of magnitude as, but of opposite sign to, the exaltations of the

molecular refractivity; the exaltation of the dispersivity is very much greater.

The thermochemical method will not displace the more convenient spectrochemical methods of investigating the constitutions of organic compounds, but will serve as a useful auxiliary. Auwers and Eisenlohr (this vol., ii, 365) have shown that a "disturbed conjugation" diminishes the exaltation of the molecular refractivity and dispersivity; in fact, the optical evidence does not establish with certainty the presence of a conjugate linking in α-phellandrene. The thermochemical method leaves no doubt about the point, since the thermal "depression" of this terpene is practically the same as those of other terpenes containing conjugate linkings.

The theory of the identity of carvenene and α-terpinene receives support from the close agreement in their heats of combustion.

The parallelism between the thermal and the optical data disappears in the case of bicyclic terpenes; the presence of a 4-ring in $d\alpha$- and β-pinenes instead of a conjugate linking does not cause any appreciable deviation of the heats of combustion from the normal value, whilst it does greatly affect the optical behaviour.

The molecular heats of combustion of the following styrene hydrocarbons have been measured; styrene, 1035 (freshly distilled), 1039 (after keeping for a few hours); β-methylstyrene, 1190; β-ethylstyrene, 1346; α-methylstyrene, 1193; $\alpha\beta$-dimethylstyrene, 1347; trimethylstyrene, 1510; $\beta\beta$-diethylstyrene, 1665; α-phenyl-Δ^{β}-butene, 1353; α-phenyl-Δ^{β}-pentene, 1510 Cal.

"Normal values" in this series are obtained as follows. The difference of the molecular heats of combustion of the two last-mentioned hydrocarbons is 157 Cal.; also, the values for styrene, β-methylstyrene, and β-ethylstyrene, all of which contain an undisturbed conjugate system, differ by 155 for the first pair and by 156 for the second pair. The mean, 156, of the three values represents the thermal value of CH_2. The heat of combustion of α-phenyl-Δ^{β}-butene, which does not contain a conjugate linking, is taken as thermally normal; by adding or subtracting 156, or multiples thereof, the normal heats of combustion of the higher and lower homologues are calculated. The variation of the actual from the normal values is much less than in the case of the terpenes, but it is again obvious that the presence of conjugate linkings is accompanied by a diminution of the heat of combustion.

In the styrene series, the presence of conjugate linkings is more accurately and simply ascertained by spectrochemical methods, but the thermochemical method is of interest, because it serves to emphasise the remarkable parallelism between the optical and the thermal properties. For example, the depression of the heat of combustion and the exaltation of the refractivity and of the dispersivity are most pronounced in styrenes with undisturbed conjugation, such as styrene itself, β-methylstyrene, and β-ethylstyrene; a simple central disturbance of the conjugate system, as in α-methylstyrene and $\alpha\beta$-dimethylstyrene, diminishes the thermal and the optical abnormalities to about one-half to two-thirds of the original values. Further lateral disturbance, as in trimethylstyrene, causes the thermal depression to vanish

and the exaltation of the refractivity to become very small, only the dispersivity retaining, as is frequently the case, a marked exaltation.

C. S.

Diazo- and Azo-compounds. Thermochemical Investigations. I. W. SVENTOSLAVSKY (*Ber.*, 1910, **43**, 1479—1488).—The following thermochemical constants have been determined: (1) Heat of diazotisation of aniline in aqueous solution = +22·8 Cal.: obtained by mixing a solution of aniline in hydrochloric acid with a solution of sodium nitrite and subtracting from the heat of the reaction the difference between the heats of neutralisation of hydrochloric and nitrous acids. (2) Heat of solution of benzenediazonium chloride = −1·84 Cal. (3) Heat of neutralisation of the diazohydroxide with hydrochloric acid = +14·26 Cal. (4) Heat of formation of the pseudo-salt, $C_6H_5N_2{\cdot}ONa$, from the diazonium chloride and sodium hydroxide solution = +5·28 Cal. (5) Heat of formation of benzeneazo-β-naphthol from the pseudo-salt and solid β-naphthol = +27·22 Cal., or $C_6H_5{\cdot}N_2{\cdot}OH$ (liq.) + $C_{10}H_7{\cdot}OH$ (solid) = $H_2O + C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$ (solid) + 27·22 Cal. (6) Heat of diazotising aniline in acetic acid solution = +23·28 Cal.; $NH_2Ph(HO{\cdot}Ac)$ (liq.) + HNO_2 (soln.) = $Ph{\cdot}N_2{\cdot}OAc$ (soln.) + $2H_2O$ + 23·28 Cal. (7) Heat of solution of aniline in acetic acid = +6·75 Cal. (8) Heat of formation of *p*-dimethylaminoazobenzene in solution from benzenediazonium acetate and dimethylaniline = +18·35 Cal., and heat of solution of *p*-dimethylaminoazobenzene in acetic acid = −3·13 Cal. (9) Heat of diazotising α-naphthylamine in aqueous solution = +24·82 Cal. Heat of formation of the pseudo-salt, α-$C_{10}H_7{\cdot}N_2{\cdot}ONa$ (soln.), from the diazonium chloride and sodium hydroxide solution = +4·84 Cal. (10) Heat of formation of α-naphthaleneazo-β-naphthol (solid) from the pseudo-salt and β-naphthol (solid) = +29·53 Cal., of the solid hydroxy-compound from the diazohydrate and solid β-naphthol = +34·69 Cal., and of the solid hydroxy-compound from a solution of the diazonium chloride and an alkaline solution of β-naphthol = +32·82 Cal. (11) The heat of formation of nitroso-β-naphthol from solid β-naphthol and nitrous acid in acetic acid solution = +28·66 Cal., or for the solid nitroso-compound = +32·47.

The heat of diazotising an amine in 50% acetic acid is somewhat greater than in glacial acetic acid, owing to the hydrolysis of the acetate of the amine in the 50% acid.

J. J. S.

Diazo- and Azo-compounds. Thermochemical Investigations. II. W. SVENTOSLAVSKY (*Ber.*, 1910, **43**, 1488—1495. Compare preceding abstract).—The heat produced in mixing a solution of sulphanilic acid with nitrous acid = +20·40 Cal. This when corrected by adding the heat of neutralisation of the diazo-compound and subtracting the heat of neutralisation of the amine gives +25·5 Cal.

$$C_6H_4{<}\genfrac{}{}{0pt}{}{SO_3}{N_2}{>} + 2NaOH = SO_3Na{\cdot}C_6H_4{\cdot}N_2ONa + H_2O + 10{\cdot}7 \text{ Cal. and}$$

$SO_3H{\cdot}C_6H_4{\cdot}NH_2 + NaOH = H_2O + SO_3Na{\cdot}C_6H_4{\cdot}NH_2 + 10{\cdot}45$ Cal., and the difference between 10·45 and the heat of neutralisation of benzene-

sulphonic acid (13·6 Cal.) gives the value of the heat of inner salt formation of sulphanilic acid.

The reaction between sulphanilic acid and sodium nitrite solution proceeds slowly, and gives +16·20 Cal., or, since the difference between the heats of neutralisation of nitrous and sulphanilic acids is 0·2 Cal., $SO_3Na\cdot C_6H_4\cdot NH_2$ (soln.) + HNO_2 (soln.) = $H_2O + SO_3Na\cdot C_6H_4\cdot N_2\cdot OH$ (soln.) +16·0 Cal.

The heat of formation of the pseudo-salt, $SO_3Na\cdot C_6H_4\cdot N_2\cdot ONa$, from a solution of the diazohydroxide and sodium hydroxide solution = +5·46 Cal.

The heat of formation of methyl-orange from dimethylaniline and diazobenzenesulphonic acid = 33·48 Cal.

The conclusion is drawn that the conversion of a diazonium hydroxide, OH·NR⋮N, into a diazohydroxide, RN:N·OH, is accompanied by little or no heat change.

The diazotising of anthranilic acid in aqueous solution gives rise to +21·42 Cal.

The heat of neutralisation of anthranilic acid by sodium hydroxide solution is +10·5 Cal., and that of *o*-diazobenzoic acid +6·56.

The heat of coupling *o*-diazobenzoic acid with *β*-naphthol in alkaline solution is +33·98 Cal., and as this value agrees with the heats of formation of hydroxyazobenzene (+32·85) and hydroxyazonaphthalene (+34·68), the conclusion is drawn that in alkaline solution the diazobenzoic acid contains a free N:N·OH group. J. J. S.

Calorimetric Observations of the Reciprocal Coagulation of Ferric Hydroxide and Silver Hydrosols. FRIEDRICH DOERINCKEL (*Zeitsch. anorg. Chem.*, 1910, **67**, 161—166. Compare this vol., ii, 269).—The two colloids used for the experiments are a 5% solution of ferric hydroxide and a solution containing 9% of metallic silver and 1% of a protective colloid. The apparatus is the same as that previously used. In each experiment, 250 c.c. of each solution are employed, and the concentration of the silver colloid is expressed as the percentage of the total colloid in the united volume of 500 c.c. The heat of dilution of both colloids with water is zero. The heat of coagulation increases with the percentage of silver colloid, reaching a maximum at 60—70%, and then falling rapidly. The optimum of coagulation does not coincide with this maximum, but corresponds with 70—80% of silver colloid. Coagulation is retarded by the presence of a large excess of either substance. The colloid used to protect the silver is without action on ferric hydroxide.

Silver hydrosol is coagulated by ammonium nitrate if the concentration of the latter exceeds 40%, and the precipitate becomes perfectly soluble after washing until free from electrolyte. The heat of coagulation is +1—2 cal. per gram of silver. Aluminium sulphate, even in 1·7% solution, causes complete irreversible coagulation, the heat of solution being negative, and due almost entirely, if not entirely, to the protective colloid. C. H. D.

Thermal Properties of Solids and Liquids. S. LUSSANA (*Nuovo Cim.*, 1910, [v], **19**, i, 182—207).—The author has inves-

tigated the compressions of a number of metals and alloys by a modification of the method previously described (*ibid.*, 1904, [v], 7, 355), the results being briefly as follows:

With aluminium the coefficient of compressibility (k) increases proportionally with rise of temperature, and the value of the coefficient of expansion (a) increases with rise of temperature and diminishes with increase of pressure. For bismuth, the values of k increase almost proportionally with rise of temperature, but at the higher temperatures diminish appreciably with increase of pressure; a increases with rise of temperature, and diminishes with increase of pressure. With antimony, k increases almost in proportion with temperature, and a increases with rise of temperature and diminishes with increase of pressure.

The compressibilities of a large number of alloys were measured, the principal results being that (1) the compressibility does not obey the law of mixtures; (2) in general, the compressibility is diminished by the initial addition of an extraneous substance; (3) the compressibility increases with rise of temperature, and the coefficient of expansion diminishes with increase of pressure. T. H. P.

Attraction Pressure. Isidor Traube (*J. Physical Chem.*, 1910, **14**, 452—470).—A résumé of the author's communications on cohesion pressure (compare Abstr., 1908, ii, 565; 1909, ii, 216, 325, and 647). T. S. P.

Theory of Attraction Pressure. Isidor Traube (*J. Physical Chem.*, 1910, **14**, 471—475).—A theoretical paper of a qualitative nature with respect to the hydrating effect of cohesion pressure. It is assumed that the molecules and ions of a solute surround themselves, similarly to the condensation nuclei of gases, with an envelope of water molecules, the intensity of attraction between the molecules (or ions) and the water envelope corresponding with the cohesion pressure. Various deductions are made which are not in accordance with the dissociation theory of Arrhenius, and the osmotic pressure theory of van't Hoff. T. S. P.

Viscosity-coefficients of Vapours and their Variation with Temperature. Karl Rappenecker (*Zeitsch. physikal. Chem.*, 1910, **72**, 695—722).—The viscosities of a number of vapours have been measured at 100° and 212° by a modification of a method described by Pedersen (*Physical Review*, 1907, **25**, 230). The values of $\eta \times 10^{-7}$ at 100° (where η is the absolute viscosity coefficient) are as follows: *iso*pentane 885·1, ethyl ether 967·1, acetone 942·7, ethyl alcohol 1090, methyl acetate 1015, ethyl acetate 954·6, chloroform 1307, benzene 930·2. From the values at 100° and 212°, the variation of the viscosity with temperature is expressed as proportional to the n^{th} power of the absolute temperature, and with the exception of chloroform and ether, which probably act on the mercury in the apparatus, the value of n is about 1·1.

The temperature-coefficients thus found are in satisfactory agreement with the formula of Sutherland, $T^{0·5}/(1 + C/T)$, where C is proportional

to the work gained when two molecules are brought into contact from a great distance, and with a somewhat similar formula obtained by Reinganum.

From the results, by means of a formula proposed by Reinganum (Abstr., 1909, ii, 223), the molecular volumes and the absolute number of molecules in a gram-molecule of vapour are calculated. The values for the molecular volumes are in excellent agreement with those determined directly by Kopp. For the absolute number of molecules in a gram-mol., the value $6{\cdot}20 \times 10^{23}$ is obtained; it is independent of the nature of the substance, as the molecular-kinetic theory requires and agrees almost exactly with that calculated from quite different premises by Planck and by Rutherford and Geiger. G. S.

Viscosity of Certain Metals and its Variation with the Temperature. CHARLES E. GUYE and SAUL MINTZ (*Arch. sci. phys. nat.*, 1910, [iv], 29, 474—475).—An amplification of the details given in a previous paper (Abstr., 1908, ii, 930). Some corrections are also made. T. S. P.

The Influence of the Reaction of the Medium on Adsorption. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, 25, 359—366).—The adsorbents employed were carbon, kaolin, and ferric hydroxide. With certain substances, it was found that the maximum of adsorption took place with a certain definite hydrogen ion concentration (albumin); in others, a minimum of adsorption took place with definite hydrogen ion concentration (amylase), whereas with a third class of substances (trypsin) a continuous change in the amount of adsorption occurred on altering the reaction of the medium, without the attainment at any time of a definite maximum or minimum.

S. B. S.

Adsorption and Colloid Precipitation. HUGO MORAWITZ (*Koll. chem. Beihefte*, 1910, 1, 301—330).—With the object of testing Freundlich's theory relative to the connexion between adsorption and colloidal precipitation, measurements have been made of the adsorption of electrolytes by animal charcoal, and also of the influence of these on the precipitation of colloidal gold solutions.

From adsorption experiments with aqueous solutions of zinc, lead, copper, silver, and mercuric salts, it is found that the magnitude of the adsorption is dependent on the nature of the cation and the anion, and on the degree of ionisation. In general, the adsorption increases as the electro-positive character of the cation diminishes. Mercuric chloride is adsorbed in exceptionally large quantities, the adsorption of the substance being thirty times as great as that of zinc chloride.

In general, the results of the coagulation experiments indicate that those salts which are most readily adsorbed by animal charcoal are the most active in bringing about the precipitation of colloidal gold. Differences in the two series of experimental data indicate, however, that the phenomena are complicated by factors which mask to a considerable extent the influence of the specific chemical nature of the electrolyte. In the case of certain salts of the heavy metals, the

coagulative capacity towards a slightly acid collodial gold solution is very much smaller than towards a feebly alkaline solution. The ratio of the two influences in the case of mercuric chloride is of the order of a thousand. H. M. D.

Relationships between Adsorption and Toxicity. WOLFGANG OSTWALD and A. DERNOSCHECK (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 297. Compare Abstr, 1906, ii, 112; 1907, ii, 981).—In a previous paper it was shown that the relationship between the concentration and the toxicity of sea-water solutions towards *Gammarus* could be approximately represented by an exponential (adsorption) formula. The necessity of taking into account the quantity of salt which is normally present in the tissue is now pointed out, and the single toxicity formula is replaced by two, one of which holds for salt solutions more concentrated than the "normal," and the other for solutions of smaller concentration.

By reference to the previous data for *Gammarus*, and new results obtained with *Daphnia magna*, it is shown that the modified toxicity formulæ are capable of representing the experimental observations more accurately than the simple exponential formula.

An explanation of the influence exerted by salts on one another when present in the same toxic solution is given on the basis of the adsorption theory. H. M. D.

The Internal Friction of Albumin Solutions. LEONOR MICHAELIS and B. MOSTYNSKI (*Biochem. Zeitsch.*, 1910, **25**, 401—416).—Horse-serum was dialysed, and after varying periods of dialysis the internal friction was measured after the addition of varying quantities of acid and alkali. If the dialysis had lasted for a sufficient length of time, a fairly sharp minimum was attained, corresponding with a hydrogen ion concentration of the order 10^{-5}. This is the isolectric point. If the dialysis had not been of sufficient duration, this minimum was less sharply defined, and a second ill-defined minimum was attained by addition of sodium hydroxide. This latter phenomena was due to an incomplete separation of the globulin. S. B. S.

The Inversion Points for a Fluid passing through a Porous Plug and their Use in Testing Proposed Equations of State. II. An Examination of Experimental Data. ALFRED W. PORTER (*Phil. Mag.*, 1910, [vi], **19**, 888—897).—The inversion points of nitrogen are calculated by a graphical method from Amagat's data, and shown to agree well with Dieterici's equation of state, but not with van der Waals'. For carbon dioxide (Amagat's values), the agreement with Dieterici's equation is again good, but the values lie on the lower, whereas for nitrogen they lie on the upper, portion of the theoretical curve. This is regarded as confirming the author's view that two inversion points exist for each pressure. For *iso*pentane, ethylene, and ethyl ether, the inversion curves are very similar to that of carbon dioxide. F. S.

Crystals which are Absolutely Stable only under High Pressures. ANTON SKRABAL (*Zeitsch. physikal. Chem.*, 1910, **73**, 171—172).—Tammann (compare Abstr., 1909, ii, 983) has pointed

out that Ostwald's rule, according to which the order of separation of forms of different degrees of stability is determined by the smallest diminution of free energy, is not valid, but the author shows that a modification of this rule proposed by him (compare *Zeitsch. Elektrochem.*, 1908, **14**, 529), according to which there is a connexion between the velocity of a change and the stability of the reaction products in such a way that the more rapid the reaction the greater is the possibility of obtaining the less stable products, is in accordance with the experimental facts. G. S.

Gelatinisation of Silicic Acid. I. NICOLA PAPPADÀ and C. SADOWSKI (*Zeitsch. Chem. Ind. Kolloide,* 1910, **6**, 292—297).—The influence of electrolytes on the gelatinisation of solutions of silicic acid and the relationship between the processes of gelatinisation and coagulation (flocculation) have been examined. Whether gelatinisation or coagulation takes place depends on the concentration of the colloidal solution, the former occurring with concentrated and the latter with more dilute solutions. The influence of different electrolytes on the velocity of the two processes is very nearly the same. From experiments with the alkali metal chlorides, it is found that the velocity increases with the atomic weight of the cation. Comparative observations with the alkaline-earth metal chlorides show that the velocity increases with the magnitude of the electric charge on the cations.

A theory is advanced in explanation of the observations, and according to this the gelatinisation effect of different ions is determined by their rates of diffusion. H. M. D.

Distribution of Iodine between Certain Organic Solvents. M. LANDAU (*Zeitsch. physikal. Chem.*, 1910, **73**, 200—211; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 377—395. Compare Waentig, this vol., ii, 117).—The distribution of iodine between glycerol and benzene and between glycerol and carbon tetrachloride has been determined at 25°, 40°, and 50°. The ratio of the concentration in benzene and in carbon tetrachloride to that in glycerol increases regularly with the iodine concentration, in agreement with the views of Beckmann and of Hantzsch and Vogt, that in solvents forming brown solutions (such as glycerol) iodine is partially combined with the solvent, whilst in violet solutions it is uncombined.

Further, the distribution of iodine between ethyl ether and ethylene glycol, both of which give brown solutions, was measured at 0° and 25°, and it was found that the distribution ratio is practically independent of the dilution. The direct determination of the distribution of iodine between two violet solutions is not possible, as all such solvents are partially or completely miscible, but the distribution between benzene and carbon tetrachloride has been calculated from the results of each with glycerol. In this case, also, the ratio is practically independent of the concentration, and the same is true for chloroform and carbon tetrachloride, also calculated indirectly. There is evidence also of partial combination in violet solutions, although to a much smaller extent than in the brown solutions.

The amount of combination in some solvents at low temperatures has been calculated on the assumption, which is only approximately true, that at high temperatures and in concentrated solutions the proportion of iodine combined is negligible. From a formula deduced on this basis, it is calculated that the proportion of iodine combined with glycerol at 25° varies from 46% to 7·6% as the concentration is increased from 0·0016 to 0·0208 mol. per litre. G. S.

The System Phenylhydrazine-Water. JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 417—425).—The melting points, boiling points, and specific gravities of various mixtures of phenylhydrazine and water have been determined.

When the results are plotted with temperatures as ordinates and percentages as abscissæ, a curve is obtained indicating that with water phenylhydrazine only forms one hydrate. On addition of water to phenylhydrazine, the m. p. falls to the eutectic point (16·6°) of phenylhydrazine + hydrate, phenylhydrazine separating out. On addition of more water, the hydrate $C_6H_5NH\cdot NH_2,\frac{1}{2}H_2O$ separates, the m. p. first rising to 26·2°, that of the hydrate, and then falling to 20·4°, when separation into two layers takes place. Between the limits 60·1% and 11·6% of phenylhydrazine, the m. p. remains constant at 19·8°. On addition of more water, the liquid becomes homogeneous, and the hydrate separates out until the eutectic point (hydrate + water) is reached at −0·7°. Ice then separates from this temperature to 0°. The shape of the melting-point curve of the hydrate indicates that it is gradually dissociated in the fused liquid.

A mixture of 30% of phenylhydrazine and 70% of water, which has been made homogeneous by warming, becomes opalescent on cooling to 57°. The opalescence increases as the temperature falls, and at 55° the liquid becomes suddenly opaque and separates into two layers. All mixtures with compositions approximating to that of the critical mixture exhibit these opalescence phenomena.

When a mixture of about 33% of phenylhydrazine and 67% of water is made homogeneous by warming to 60—65°, agitation produces considerable foaming. This foaming vanishes at 55°, its disappearance coinciding with the appearance of two layers. On cooling to 45°, the heterogeneous liquid regains its property of foaming, and retains it to about 10°, when the hydrate crystallises out, yielding a thick deposit full of air bubbles. All mixtures containing 40% to 15% of phenylhydrazine exhibit this phenomenon. Mixtures with about 10·9%, and also 40—60%, of phenylhydrazine do not foam in the heterogeneous region.

For mixtures of phenylhydrazine and water, the liquid and vapour curves do not approach at the concentration of the hydrate, indicating complete dissociation of the hydrate in the state of vapour. The curves also indicate that the principal product of the initial part of the distillation is water, the b. p. of the residual liquid only rising slightly. When most of the water has passed over, the b. p. rises rapidly to that of phenylhydrazine.

The densities of mixtures of phenylhydrazine and water give no indication of the formation of a hydrate. A. J. W.

Influence of the Solvent on the Equilibrium Constant. LEO PISSARJEWSKY and I. BELENOWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 530—536. Compare Pissarjewsky and Trachoniotowsky, this vol., ii, 402) —The authors have measured the constant $K = C^{Ag(CN)_2}/C_{Cl}$ of the reaction $2AgCN + KCl = KAg(CN)_2 + AgCl$ at 25° in water, 10·5% aqueous mannitol, and 23·7% aqueous glycerol, the results, together with the values of η for the different solvents, being as follows :

	K.	η.
Water	0·030	1·00
10% mannitol solution	0·027	1·36
23·7% glycerol ,,	0 029	1·95

The value of K is hence practically independent of the solvent, in spite of the considerable variation of the viscosity (compare Lucas, Abstr., 1904, ii, 715).

Similar measurements were made of $K = C_{Ag(CN)_2}/C_{Br}$ for the reaction : $2AgCN + KBr \rightleftarrows KAg(CN)_2 + AgBr$ at 25° in aqueous solutions of various alcohols, the results being as follows :

	K.	η.
30% glycol solution	8·8	2·02
20% erythritol solution	5·9	1 61
50% methyl alcohol solution	7·15	1·62

Here, again, no relation exists between K and η. T. H. P.

Influence of Insoluble Salts in Equilibria. LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 536—537).—According to Laschtschenko (*Trans. Phys. Chem. Soc. Kharkoff Univ.*, 1908, **35**, part 21), the course of a reversible heterogeneous reaction in a solvent is influenced distinctly by the degree of solubility of sparingly soluble salts and by a change of this solubility in relation to changes in composition and concentration of the liquid phase of the system. The author's results (Abstr., 1909, ii, 866 ; this vol., ii, 402, and preceding abstract) give no indication of any such influence. T. H. P.

Free Energy of Chemical Action in Mixtures of Water with Non-electrolytes. III. LEO PISSARJEWSKY and K. ZEMBISKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 537—544).—The authors have measured the constant $K = C_{Ag(CN)_2}/C_{Br}$ of the reaction $2AgCN + KBr \rightleftarrows KAg(CN)_2 + AgBr$ at 25° in water, for which Lucas (Abstr., 1904, ii, 715) found the value 7·1, and in aqueous solutions of various non-electrolytes, and have calculated the corresponding values of the free energy of the reaction by means of the equation : $A = RT\log K$. The numbers obtained, which, together with those of η, are given in the following table, show that no relationship of a general character exists between the value of η for any solvent and the values of K and A for a reaction taking place in that solvent.

	K.	A.	η.
Water	8 1	1270 cals.	1·0
10·5% mannitol solution	6·6	1121 ,,	1·36
9 8% glycerol solution	6·5	1110 ,,	1·3
23·7% glycerol solution	9·3	1322 ,,	1·95
49·9% glycerol solution	11·5	1450 ,,	5·5
50·0% acetone solution	6·9	1146 ,,	1·25
75 0% methyl alcohol solution	21·0	1798 ,,	0·86

The empirical formula, $A = A_b - 100B.\eta$, deduced by Pissarjewsky and Levites (Abstr., 1908, ii, 570), is found to be inapplicable in this instance. There exist, however, indications of an empirical relation between A and η for a particular group of solvents, such as aqueous solutions of glycerol, probably owing to the formation of a definite compound between the solvent and the solute. The fact that the reaction proceeds in either direction more slowly in 50% acetone or 74% methyl alcohol than in 50% glycerol is also a probable indication of the formation of compounds between the ions of the dissolved compounds and the molecules of the solvent. T. H. P.

Equilibria in Ternary and Quaternary Systems in which Two Liquid Layers Occur. F. FONTEIN (*Zeitsch. physikal. Chem.*, 1910, **73**, 212—251).—The data required for the construction of the complete equilibrium diagram for the system amyl alcohol–ethyl alcohol–water–sodium chloride have been determined, and some measurements have also been made with methyl instead of ethyl alcohol.

The equilibrium between the liquid phases in the system amyl alcohol–ethyl alcohol–water has been determined by solubility measurements according to Alexéeff's method, and from the results, the binodal curves for 0°, 15·5°, and 28° are constructed in the usual way. It can be deduced from the graphic representation that when ethyl alcohol is slowly added to a saturated aqueous solution of amyl alcohol at 0°, a separation into two layers at first occurs, but later the mixture becomes homogeneous; at 15·5° and 28° no separation occurs. hese conclusions have been confirmed by experiment.

The position of conjugate points on the diagram has been determined by the separate analysis of two layers in equilibrium. The special methods used are fully described. The critical solution at 15·5° contains 20% of amyl alcohol, 27% of ethyl alcohol, and 53% of water; at 28° it contains 20% of amyl alcohol, 25% of ethyl alcohol, and 55% of water. The composition of the critical solution can also be derived from the distribution coefficients of the components.

Similar experiments have been made with methyl alcohol instead of ethyl alcohol, and the corresponding binodal lines for the two systems are compared.

As regards the equilibrium water–amyl alcohol–sodium chloride, a number of conjugate layers were prepared at 28° and analysed. In the upper layer, which consists of a saturated solution of water in amyl alcohol, very little sodium chloride dissolves.

A number of solubility determinations were also made at 28° with the four components in order to fix some further points of the complete equilibrium diagram. The results are also given in tabular form.

G. S.

Rate of Decomposition of Barium Ethyl Sulphate in Acid and Alkaline Solutions at Different Temperatures. ROBERT KREMANN (*Monatsh.*, 1910, **31**, 165—176).—The reaction between barium ethyl sulphate and water may be represented by the equation:

$Ba(SO_4Et)_2 + 2H_2O = BaSO_4 + H_2SO_4 + 2EtOH$ (1), but the sulphuric acid thus formed reacts with more of the barium salt, $H_2SO_4 + Ba(SO_4Et)_2 = BaSO_4 + 2HEtSO_4$ (2), so that the total reaction is $2Ba(SO_4Et)_2 + 2H_2O = 2BaSO_4 + 2EtOH + 2HEtSO_4$ (3). But in addition to this, the ethyl hydrogen sulphate is slowly decomposed by the water, yielding ethyl alcohol and sulphuric acid, the latter then reacting with the barium salt, $HEtSO_4 + H_2O + Ba(SO_4Et)_2 = BaSO_4 + EtOH + 2HEtSO_4$ (4).

The rate of decomposition of the barium salt with pure water and with 0·5*N*- and *N*-solutions of hydrochloric acid has been determined at 55° and 66° by weighing the amount of barium sulphate formed after given intervals of time. The curves show that with *N*-hydrochloric acid the decomposition is more rapid than with water, but that with 0·5*N*-acid the rate of decomposition is considerably slower than when water alone is used. This may be due to the fact that the reaction represented by equation (3) is retarded by the presence of hydrions, whereas the reaction (4) is accelerated by hydrions. With very dilute acid, the retarding action is the more pronounced, but with more concentrated acid the accelerating action becomes so. This is supported by the fact that in aqueous solutions the decomposition is less the more concentrated the solution.

Similar experiments have been made with standard solutions of sodium hydroxide. The sodium ethyl sulphate formed is stable, and is not hydrolysed to any appreciable extent by the alkali. The decomposition proceeds more slowly than in neutral solution, and the rate increases roughly proportionally to the concentration of the alkali. At the beginning, the reaction is practically unimolecular, but the value of K diminishes as the alkali is used up. J. J. S.

Kenetics of the Decomposition of Quaternary Ammonium Salts in Chloroform Solution. EDGAR WEDEKIND and F. PASCHKE (*Zeitsch. physikal. Chem.*, 1910, **73**, 118—128. Compare Abstr., 1908, i, 334).—The rate at which certain quaternary ammonium salts of the type NR_4X, where X represents a halogen atom, decompose in chloroform solution according to the equation $NR_4X = NR_3 + RX$ is represented in the first instance by an equation of the first order, but the "constants" increase somewhat during the reaction, and are the greater the smaller the initial concentration. This is now shown to be due to partial polymerisation to double molecules in chloroform solution; only the simple molecules undergo decomposition.

The experiments were made with propyl- and allyl-phenylbenzylmethylammonium bromides. The degree of polymerisation in different dilutions was determined from the results of distribution measurements between water and chloroform at 25° in the usual way, a correction being applied on account of the fact that the salts are partly ionised in aqueous solution. In connexion with the last-mentioned point, the molecular conductivities of the salts were determined in water (and also in absolute alcohol) at 25°.

The rate of decomposition of *d*-phenylbenzylmethylpropylammonium iodide is diminished by addition of the corresponding nitrate. G. S.

Catalysis in Heterogeneous Systems. The Equilibrium $Ti^{III} + H^{\cdot} \rightleftarrows Ti^{IV} + H$, and the Reaction $HCN + 2H_2 = CH_3 \cdot NH_2$. HENRY G. DENHAM (*Zeitsch. physikal. Chem.*, 1910, **72**, 641—694).—It has been shown by Diethelm and Foerster (compare Abstr., 1908, ii, 350) that in sulphuric acid solution there is an equilibrium between tervalent and quadrivalent titanium, represented by the equation $Ti^{\cdot\cdot\cdot} + H^{\cdot} \rightleftarrows Ti^{\cdot\cdot\cdot\cdot} + H$, and that in the presence of platinised platinum the equilibrium can be reached from both sides. The position of the equilibrium under varying conditions and the kinetics of the two reactions have now been investigated by the author. As catalyst, platinised platinum net in the form of a cylindrical stirrer, driven at constant speed, was used. Except when otherwise mentioned, the solutions contained excess of sulphuric acid; in the majority of cases the acid was normal.

The position of the equilibrium depends on the pressure of the hydrogen. At 638 mm. pressure and 25°, the equilibrium mixture contains about 38·7% of quadrivalent titanium; at 416 mm., 43·5%, and at 209 mm., 61·1%. Rise of temperature also favours the production of $Ti^{\cdot\cdot\cdot\cdot}$; at 35° the equilibrium mixture contains 42%, and at 45° 49%, of quadrivalent titanium.

The reversible reactions, $Ti^{\cdot\cdot\cdot} + H^{\cdot} \rightleftarrows Ti^{\cdot\cdot\cdot\cdot} + H$, were followed by measuring the rate of the appearance and disappearance of hydrogen respectively, and, apart from some initial disturbances, are both unimolecular. Variation of the hydrogen pressure between 10 and 76 cm. had practically no effect on the reaction velocity. The temperature-coefficient of the reaction-velocity is only 1·29 for an increase of 10°, and for this and other reasons, the conclusion is drawn that the speed of the reaction is determined by the rate at which the reacting substances diffuse to the platinum surface.

When the position of the equilibrium is determined from the amount of hydrogen absorbed instead of by the more trustworthy method of titration with permanganate, different results are obtained, and it is suggested that the excess of hydrogen taken up is due to the presence of higher compounds in which the titanium is quinquevalent or sexavalent.

The rate of the reaction when titanium chloride and hydrochloric acid is used is very nearly the same as with the sulphate, but the position of equilibrium in the two cases is different. In $N/1$-hydrochloric acid the equilibrium mixture contains 53%, in $2N$-acid about 26·6%, of quadrivalent titanium.

Hydrocyanic acid does not retard the action of platinum in this case, but in acid solution under the conditions of the experiment is completely reduced to methylamine.

In connexion with the conclusion that the speed of the reaction is determined by a diffusion process, the general question of reaction velocities in such heterogeneous systems is discussed, and it is suggested that the high concentration of the reacting substances on the surface of the platinum, due to adsorption, is of considerable importance in this connexion (compare Nernst and Brunner, Abstr., 1904, ii, 315; Sand, Abstr., 1905, ii, 233; Senter, *ibid.*, ii, 377, 379;

Teletoff, Abstr., 1906, ii, 95; Bayliss, Abstr., 1906, ii, 344; Lewis, Abstr., 1909, ii, 383). G. S.

Specific Stereochemical Behaviour of Catalysts. KASIMIR FAJANS (*Zeitsch. physikal. Chem.*, 1910, **73**, 25—96).—Part of the work described in the paper has already been published (compare Abstr., 1908, ii, 268). The rate of elimination of carbon dioxide from the optically active camphorcarboxylic acids has also been studied in acetophenone solution in the presence of a number of alkaloids. With quinine, the *l*-acid decomposes 46% faster than the *d*-acid, and with quinidine, the *d*-acid decomposes 46% faster than the *l*-acid. The differences between the rates of decomposition of the two acids in the presence of other alkaloids are less pronounced.

The fact that the rate of reaction of the free acids is much less than when bases are added is ascribed to salt formation, the salts being decomposed much more readily than the free acids. There is evidence, however, that in some cases salt formation is not complete, but an equilibrium exists, represented by the equation: $C_{base}C_{acid}/C_{salt} = K$, and some of the deviations from a simple unimolecular reaction are thus accounted for. The temperature-coefficient for 10° for the reaction between 80° and 90° is about 3·1 in water, benzene, and acetophenone. The velocity of decomposition of the inactive acid in the absence of a base is about 3% less than that of the active acids, indicating the presence of a small proportion of the racemic acid.

A few preliminary experiments with bromocamphorcarboxylic acids show that the rate of decomposition in the presence of an equivalent amount of quinine or quinidine is about two thousand times greater than that of the free acids under equivalent conditions.

The optical activation of inactive camphorcarboxylic acid has been brought about by heating with quinine until partial decomposition has occurred, and then interrupting the action. As anticipated, the unchanged acid was slightly dextrorotatory, the camphor formed slightly lævorotatory. Corresponding results were obtained with quinidine.

Bodenstein (*Zeitsch. Elektrochem.*, 1909, **15**, 394) has pointed out that the acceleration of the decomposition of an acid by addition of a base, resulting in salt formation, can scarcely be regarded as an example of catalysis, but the author points out that it is in accordance with Ostwald's definition of a catalytic action, the base in this case remaining unaltered at the end of the experiment.

The theoretical bearings of the results, more particularly with reference to asymmetric syntheses by catalysis, and to analogies with the specific action of enzymes, are discussed in great detail, with numerous references to the literature of the subject. The specific behaviour of the enzymes to optical isomerides is only quantitative in character, as the capacity to combine with an enzyme is not confined exclusively to one of the optical antipodes. Suggestions are made to account for the peculiarities in the synthetic action of enzymes on the sugars. G. S.

Atomic Weight Accurately a Function of the Volution of Ideal Space-Symmetry Ratios. NEWMAN HOWARD (*Chem. News*, 1910, **101**, 265).—A restatement of views expressed previously in reference to the connexion between atomic weight values and certain geometric ratios (compare this vol., ii, 490). H. M. D.

The Periodic System. A. VOSMAER (*Chem. Weekblad*, 1910, **7**, 483—484).—A criticism of the periodic table, pointing out that it does not indicate any relation between atomic weights and electrical conductivity, melting point, hardness, or changing valency.
A. J. W.

Radius of the Sphere of Action of a Molecule. R. D. KLEEMAN (*Phil. Mag.*, 1910, [vi], **19**, 840—846).—The radius of the sphere of action of a molecule is deduced by means of theoretical expressions from the surface-tension of the liquid and the latent heat of evaporation and their change with temperature. Values of the former are obtained from the work of Ramsay and Shields, and of the latter from that of Mills. The results for a number of carbon compounds indicate that the diameter of the sphere of action is very nearly of the same magnitude as the distance of separation of the molecules in a liquid. It is further deduced that the factor expressing the variation of the diameter of the sphere of action with temperature must have the same value for all liquids at corresponding states, and that the values of $\lambda/\rho L$ (λ is the surface-tension, ρ the density, and L the latent heat of evaporation) for all liquids at corresponding temperatures should be constant, and are approximately so. F. S.

Experimental Illustration of the Law of Multiple Proportions. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1910, **43**, 553—556).—The following is recommended as a lecture experiment to demonstrate the law of multiple proportions. Finely-powdered cuprous chloride (0·1—0·25 gram) is weighed in a porcelain boat, which is afterwards placed in a combustion tube and heated in a gentle current of chlorine until the weight is constant The boat is allowed to cool to a certain extent in the stream of chlorine, and is then transferred to a weighing bottle, which is allowed to cool in a desiccator and is afterwards weighed. The anhydrous cupric chloride is dissolved in water, and the copper estimated either by electrolysis or by precipitation with zinc. It is found that the conversion of the cuprous chloride into the cupric salt and the weighing of the cupric chloride can be completed and the estimation of the copper begun in one hour. The estimation can be finished and the copper weighed at the next lecture. E. G.

Clearing of Emulsions. RICHARD FANTO and MILAN J. STRITAR (*J. pr. Chem.*, 1910, [ii], **81**, 564—568).—In this preliminary paper the authors describe a method whereby emulsions can be electrically cleared. With a continuous current (at 220 volts and a lamp resistance) the two wires, touching below the surface of the emulsion, are moved about in the liquid, which is thereby cleared. When a spark discharge is employed, one terminal of the induction coil is connected

to a wire round the neck of a separating-funnel, the edge of which is moistened with water or other conductor; the other terminal is connected with the loop of a wire passing through the cork closing the funnel and dipping into the emulsion contained therein. C. S.

Ultra-filtration. F. J. J. Buytendyk (*Chem. Weekblad*, 1910, **7**, 425—431).—An account of previous work on filtration under pressure through porous clay saturated with gelatin or silicic acid. The author finds that a freshly-prepared solution of hæmoglobin is kept back by a 4%-gelatin filter, but not after some days. Another filter retained hæmoglobin in serum, but allowed hæmoglobin from the alimentary canal of the leech to pass. A 5%-gelatin filter retained hæmoglobin, but not the alkaline hæmatin derived from it. Serum-globulin containing 0·75% of sodium chloride is kept back by a 5%-filter, the ultra-filtrate containing 0·67% of the chloride. When this globulin solution was diluted so as to contain 0·25% of salt, the ultra-filtrate contained 0·24%. At a dilution of 0·125%, the ultra-filtrate contained the same proportion (0·125%). A. J. W.

Automatic Washing Apparatus. Ach. Grégoire (*Bull. Soc. chim. Belg.*, 1910, **24**, 223—224).—The apparatus consists of three parts, namely, a large Mariotte's bottle containing the wash-water, a funnel containing the substance to be washed, and a second funnel situated below the first and containing a siphon fitted into the neck. The shorter limb of another siphon tube reaches to the bottom of the Mariotte bottle, the longer limb ending a few millimetres above the opening of the siphon in the lower funnel. The side tubulure of the Mariotte bottle is fitted with a tube which opens on to the first funnel.

The action is as follows: wash-water runs on to the first funnel from the side-tube of the bottle. The filtrate runs into the lower funnel, and, as soon as it rises to the level of the siphon tube from the Mariotte bottle, air is prevented from entering the latter, and the flow of wash-water is stopped. The filtrate finally rises above the level of the siphon in the lower funnel, which immediately empties itself, thus again admitting air to the Mariotte bottle and allowing more wash-water to flow into the first funnel, and so on. T. S. P.

Improved Siphon. C. A. Jacobson and S. C. Dinsmore (*J. Amer. Chem. Soc.*, 1910, **32**, 810—811).—A siphon is described, consisting of a pipette bearing a side-arm from the bulb, which is bent parallel to the pipette and dips into the flask containing the liquid to be siphoned. A rubber bulb is attached to the upper end of the pipette, and a piece of rubber tubing carrying a spring-clip is fitted to the lower end. The rubber bulb is compressed, and the clip is closed. On gently diminishing the pressure on the bulb, liquid is drawn into the pipette, so that on releasing the clip the siphon will act. The apparatus is simple and easy to manipulate, is specially adapted to cases of extraction with non-miscible solvents, and is also useful for decanting the supernatant liquid from precipitates. It is very convenient for the filtration of colloidal solutions, and, in such cases, the flow through

the siphon is regulated by means of a chip of wood to hold the spring-clip open so that the rate of flow through the siphon is equal to that through the filter. E. G.

Apparatus for Drying Flasks, etc. CHARLES BASKERVILLE and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1910, **32**, 650—651).—Dry air entering a vertical tube near the bottom is heated by a red-hot platinum wire wound round an inner porcelain tube at the top of the apparatus. The hot air which streams out from small apertures at the top dries the flasks, beakers, test-tubes, etc., placed over the tube. Electricity is the source of heat employed. The platinum wire in the coil is of three different diameters, the thinnest at the lowest part and the thickest at the top of the coil; by this arrangement the coil glows with nearly uniform brightness throughout its length. L. DE K.

An Automatic Toepler Pump Designed to Collect the Gas from the Apparatus being Exhausted. BERTRAM D. STEELE (*Phil. Mag.*, 1910, [vi], **19**, 863—868).—A modified form of Toepler pump which can be automatically worked by a water pump for a long period, and enables samples of the extracted gas to be obtained when desired, whilst if needful, the whole of such gas can be collected for examination. F. S.

Preparation of Illuminating Gas as a Lecture Experiment. NICOLAE TECLU (*Chem. Zeit.*, 1910, **34**, 523).—The upper end of a Landsiedl spiral glass condenser (*B*) is fitted with a cork carrying a glass tube (*C*) holding a fish-tail burner. The lower end of the condenser is prolonged by fusing to it a T-piece having a short side-arm. To the latter is attached a hard glass test-tube (*A*) packed with small pieces of coal or wood. The remaining free end of the T-piece is fitted with a cork carrying a test-tube (*D*). On heating *A*, coal gas, water vapour, and tar are produced. The tar condenses in *D*. The water vapour is condensed in *B*, and also falls into *D*, whilst gas issues through *C* and may be burnt. T. A. H.

Inorganic Chemistry.

Solidification of Fused Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1910, 72, 752—759).—The author (compare Abstr., 1908, ii, 677—800) and others have assumed that when a homogeneous fluid mixture of S_μ and S_λ is allowed to cool, S_λ (crystalline sulphur) at first separates pure from the liquid, whilst Kruyt (Abstr., 1909, ii, 802) has suggested that mixed crystals are formed. The author now shows by microscopic observations of very thin layers of solidified sulphur that his former assumption is justified. The paper is illustrated by microphotographs. G. S.

Elastic Sulphur Resembling India Rubber. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 474—476. Compare this vol., ii, 496).—When sulphur at above 400° is poured in a thin stream into liquid air, it is obtained in the form of a thin thread of diameter 0·5—1 mm. When removed from the liquid air, this thread is quite hard and brittle, but, when the temperature rises somewhat, it assumes extraordinary elasticity. This sulphur has a polished surface, and appears pale grey in reflected light and pale yellow in transmitted light, being completely transparent and without sign of opalescence. The maximum extension of a thread about 1 mm. in diameter is approximately 5·5 times the original length, and if the extension is less than the maximum, the thread is able to return almost to its original length. The elasticity is lost in about half an hour after the thread is removed from the liquid air, the sulphur then becoming plastic and remaining so for about twenty-four hours.

T. H. P.

Electrolytic Oxidation of Sulphurous Acid in Aqueous Solution. Arthur Fischer and G. Delmarcel (*Bull. Soc. chim. Belg.*, 1910, **24**, 236—237).—A divided cell was used, the cathode, a nickel cylinder, or else a platinum spiral being contained in a porous cell. The anode was a cylinder of platinum gauze, and surrounded the porous cell; the area was 140—150 sq. cm. The catholyte was a solution either of sulphuric acid or of sodium sulphite, the anolyte being an aqueous solution of sulphur dioxide, varying in concentration from 1 to 5%. In most cases the strength of current was 1 ampere.

Catalysts, such as copper acetate, do not increase the yield of sulphuric acid, since the platinum of the electrode acts as the catalytic agent. Better results are obtained with low than with high concentrations of the electrolyte. When oxygen begins to be liberated at the anode, there is a sudden drop in the current strength.

T. S. P.

Degree of Ionisation of Sulphuric Acid in Mixtures of Alcohol and Water. Robert Kremann and Walter Brassert (*Monatsh.*, 1910, **31**, 195—200).—The degree of ionisation of sulphuric acid in various mixtures of alcohol and water has been determined by the electrical conductivity method.

As a rule, the ionisation increases with rise in temperature, except in the case of very dilute solutions and of solutions containing much water, when it diminishes with rise of temperature. The latter may be due to experimental errors, and in no case is the effect of temperature marked.

Three curves are given showing the relationship between the degree of ionisation at 0° and the concentration of the acid for the three mixtures containing 0·8%, 6·2%, and 15·4% of water.

With dilute solutions up to 0·5 mol. per litre, the alteration of the ionisation with the water contents is quite normal, for example, shows a gradual increase as the amount of water increases. With more concentrated solutions (0·5—1·4 mols. per litre) it is found that the

solutions containing only 0·8% water have a higher degree of ionisation than those containing 6·2% of water.

Curves are also given showing the relationship between degree of ionisation and amount of water present for solutions containing respectively 0·2, 0·5, and 1·0 mol. of acid per litre.

With the 1·0 mol. solution, the addition of water first diminishes and then increases the degree of ionisation. The somewhat abnormal values obtained when only small amounts of water are present are attributed to the existence of a hydrate, H_2SO_4,H_2O. J. J. S.

Atomic Weight of Tellurium. WILLY MARCKWALD and A. FOIZIK (*Ber.*, 1910, **43**, 1710—1721).—From determinations of the loss of weight of telluric acid when converted into tellurium dioxide, Marckwald has previously deduced the atomic weight of tellurium to be 126·85 (Abstr., 1908, ii, 33), which number is considerably lower than that usually accepted (127·5). The authors have further investigated the matter, using as the material, tellurium dioxide prepared from telluric acid, which had been recrystallised several hundred times. The tellurium dioxide was analysed volumetrically, being oxidised to telluric acid by potassium permanganate, and the excess of the latter determined by means of oxalic acid. The reaction was carried out either by Brauner's method (Trans., 1891, **59**, 250) in alkaline solution, or by Gooch and Howland's method (Abstr., 1895, ii, 30) in acid solution. The method of Norris and Fay (Abstr., 1898, ii, 404), in which the excess of permanganate is determined iodometrically, was also used, being modified, however, by the addition of sodium acetate in order to prevent the reversible reaction between telluric and hydriodic acids taking place. The method of Gooch and Peters (Abstr., 1900, ii, 45) was found to be unsatisfactory.

The mean result for the atomic weight of tellurium is 127·61. Marckwald's abnormal results (*loc. cit.*) are accounted for by assuming that the telluric acid ($H_2TeO_4 + 2H_2O$) used contained a small quantity of a higher hydrate in solid solution.

The authors have not been able to obtain satisfactory results with the method of Baker and Bennett (Trans., 1907, **91**, 1849), in which a mixture of tellurium dioxide and sulphur is heated in a current of nitrogen, whereby the dioxide is reduced to tellurium, and the sulphur oxidised to dioxide. It is shown that some sulphur trioxide is also formed. This formation of sulphur trioxide may account for the bad results obtained by Berzelius in the determination of the atomic weight of arsenic by making use of the reaction:

$$2As_2O_3 + 9S = 2As_2S_3 + 3SO_2.$$

T. S. P.

[Methods of Demonstrating the Properties of Liquid Air; the Collection of Atmospheric Nitrogen; and the Action of Sodium on Water.]. H. REBENSTORFF (*Zeitsch. Physik-chem. Unterr.*, 1910, **23**, 28—32, 39—40, 43—44).—An account of methods employed by the author for demonstrating the properties of liquid air; collecting atmospheric nitrogen by passing air over heated magnesium with formation of magnesium nitride; and a sketch with description of the action of sodium when placed on wet blotting paper under a bell jar. F. M. G. M.

New Compounds of Nitrogen with Metals and their Stability in the Light of the Periodic System. FRANZ FISCHER and FRITZ SCHRÖTER (*Ber.*, 1910, **43**, 1465—1479).—The method used was the formation of an arc between a silver anode and a cathode of the metal to be investigated; the electrodes were immersed in a liquid mixture of 90% argon and 10% nitrogen. The nitrides are formed by the interaction at high temperatures of the metallic vapours in the arc with nitrogen, and are preserved by the sudden cooling in the liquid gases.

The nitrides obtained were those of sodium, potassium, rubidium, cadmium, indium, thallium, lead, arsenic, antimony, tellurium, manganese, zinc, mercury, tin, and bismuth; of these, only the last five have been prepared previously. They are all true nitrides, and not derivatives of hydrazoic acid. They were never obtained quite pure, in most cases being contaminated by excess of the disintegrated metal and thereby coloured black. In the case of antimony nitride, evidence was obtained that it has the formula SbN. In all cases treatment with acids gave ammonium salts, no hydrazine salts or such like being formed.

The nitrides of metals with high atomic weights, for example, those of cadmium, mercury, lead, and bismuth, are explosive. The others decompose on careful heating, either with a slight puff, or else quietly.

With an arc discharge in gaseous nitrogen, zinc, cadmium, lead, bismuth, and nickel do not form nitrides. Tin and antimony give only traces of nitrides, whereas manganese readily forms the nitride (compare Arons, Abstr., 1900, ii, 143).

With the exception of the first group of the Periodic System, where exceptions occur, the left-hand columns of each group contain only metals which form nitrides stable at room temperature; the right-hand columns contain only metals which give nitrides that are unstable at room temperature and are decomposed either by shock or by heating. Gold, nickel, cobalt, and the platinum metals do not appear to form nitrides. T. S. P.

Solid Hydrates of Ammonia. II. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1910, **32**, 748—749).—In an earlier paper (Abstr., 1909, ii, 726) the freezing-point curve was given for the system ammonia–water which proved the existence of two hydrates: NH_3,H_2O and $2NH_3,H_2O$. The work has now been repeated with additional precautions to ensure accuracy, and the results of the previous work are confirmed. The eutectic points are: H_2O–NH_3,H_2O (not determined); NH_3,H_2O–$2NH_3,H_2O$, $-87°$, with 56·5% NH_3; and $2NH_3,H_2O$–NH_3, $-94°$, with 80% NH_3. E. G.

Hydrazine Silicofluoride and Hydrazine Titanofluoride. ERICH EBLER and E. SCHOTT (*J. pr. Chem.*, 1910, [ii], **81**, 552—556. Compare Abstr., 1908, ii, 1029).—*Hydrazine silicofluoride*,

$$(N_2H_4)H_2SiF_6,$$

m. p. 186° (decomp.), is precipitated by the addition of alcohol to a mixture of equal molecular quantities of 50% aqueous hydrazine

hydrate and 20% silicofluoric acid. It is easily soluble in water, and yields silicon tetrafluoride and hydrazine dihydrofluoride (Abstr., 1891, 263) when distilled in a vacuum.

Hydrazine titanofluoride, $(N_2H_5)_2TiF_6,2H_2O$, is prepared by dissolving titanium dioxide in cold fuming hydrofluoric acid in the proportions required to form titanofluoric acid, adding 50% aqueous hydrazine hydrate until the mixture is just alkaline, and evaporating the clear solution in a vacuum over sulphuric acid. C. S.

Oxidising Action of Ultra-violet Light on Gases. Peroxidation of Oxides of Nitrogen and Sulphur. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **150**, 1517—1520. Compare this vol., i, 349).—Nitrogen and oxygen do not combine under the influence of light from a quartz-mercury lamp. Nitrous and nitric oxides are decomposed into their elements, but in each case a portion of the gas unites with oxygen to form higher oxides. A mixture of nitrous oxide and oxygen behaves in a similar fashion.

When 2·38 c.c. of sulphur dioxide were exposed over mercury for three hours to the action of the lamp (110 volts), a contraction of 0·18 c.c. was observed, and the mercury became encrusted with a sulphate, sulphur being deposited on the sides of the tube. A mixture of sulphur dioxide and oxygen behaved in the same way, sulphur being deposited, although oxygen remained in excess. W. O. W.

Application of the Laws of Eutectics to Definite Chemical Compounds. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 428—434).—The author has applied Flawitzky's law concerning eutectic alloys (Abstr., 1906, ii, 152) to the following cases of definite chemical compounds.

(1) $PNCl_2$ forms a number of polymerides. Assuming that $(PNCl_2)_5$ represents a eutectic compound of the two neighbouring polymerides, thus: $(PNCl_2)_4 + (PNCl_2)_6 = 2(PNCl_2)_5$, the equation $n_0 = \sqrt{pM_1T_1}/\sqrt{qM_0T_0}$ (*loc. cit.*) gives the value 0·9553 instead of 1 for the ratio between the number of mols. of $(PNCl_2)_4$ and $(PNCl_2)_6$ present in the eutectic compound $(PNCl_2)_5$. The above equation gives the m. p.'s 133° and 62° respectively for the unknown polymerides $(PNCl_2)_2$ and $(PNCl_2)_8$.

(2) Flawitzky's equation is also in agreement with the view that PI_3 is a eutectic compound formed from P_2I_4 and I_2 according to the equation: $P_2I_4 + 2I = 2PI_3$, the two constituents being polymerised to the same degree. Similar agreement is found for the cases represented by the equations: (3) $2NS + 3S = N_2S_5$, the components being equally polymerised; (4) $N_2H_4 + H_2O = N_2H_4,H_2O$, the components being polymerised in the ratio $(H_2O)_2 : N_2H_4$; (5) $AsI_3 + 2I = AsI_5$, where the relative polymerisation of the constituents is represented by

$$(AsI_3)_2 : (I)_3;$$

(6) $Te + TeCl_4 = 2TeCl_2$, the relative polymerisation being

$$(Te)_2 : (TeCl_4)_5;$$

(7) $SbI_3 + 2I = SbI_5$, the constituents being polymerised in the eutectic

compound, thus, $(SbI_3)_2:(I)_5$; it is evident that if arsenic and antimony tri-iodides form a eutectic alloy, the latter should contain them in the proportions $(AsI_3)_5:(SbI_3)_3$; (8) $P_2S_5+3PCl_5=3PSCl_3$, where the relative polymerisation of the components is represented by

$$(P_2S_5)_5:(PCl_5).$$

T. H. P.

The Reciprocal Transformations of Ortho-, Pyro-, and Meta-phosphoric Acids on Heating. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1910, **67**, 234—241).—The formation of pyrophosphoric acid as the first product of the dehydration of orthophosphoric acid is due to the presence of the double molecule $(H_3PO_4)_2$. The temperatures at which pyro- and meta-phosphoric acids are formed may be raised by increasing the pressure of water-vapour in contact with the acid. If the temperature reaches that at which the double molecules of orthophosphoric acid dissociate, the meta-acid should be formed directly without the production of pyrophosphoric acid.

The acid is heated in a platinum vessel, and air is passed through the apparatus, the proportion of water vapour being regulated by bubbling the air through sulphuric acid or water at a fixed temperature. With an increasing proportion of water-vapour, the temperature at which the pyro-acid is formed increases more rapidly than that of the meta-acid, but it is not found practicable to follow the two curves to their intersection, on account of the volatility of metaphosphoric acid at high temperatures. C. H. D.

Action of Air on Coal. P. MAHLER (*Compt. rend.*, 1910, **150**, 1521—1523. Compare Boudouard, Abstr., 1909, ii, 234).—When air is passed over dry coal, free from occluded gases, at 25—30°, water, carbon dioxide, and carbon monoxide are slowly produced, the amount increasing as the temperature is raised. Less carbon monoxide is formed if the coal contains moisture. At 125°, the condensed water contains traces of hydrocarbons, and at 150° has acquired an odour of acetic acid. W. O. W.

Action of Heat on Carbon Monoxide from a Geological and Chemical Standpoint. ARMAND GAUTIER (*Compt. rend.*, 1910, **150**, 1383—1388).—Volcanic gases contain hydrogen, nitrogen, carbon monoxide, carbon dioxide, water, hydrogen sulphide, hydrogen chloride, ammonia, and methane.

On account of the dissociative action of heat, carbon dioxide, water, hydrogen chloride, and hydrogen sulphide cannot come from any great depth as such. All lavas contain ferrous silicate, which at its melting point (1250—1300°) is able to reduce water to hydrogen and carbon dioxide to monoxide. Whether hydrogen and carbon monoxide interact to give methane, and whether direct union of hydrogen and nitrogen yields ammonia, or whether metallic carbides and nitrides are the source of the methane and ammonia cannot be decided. With the object of throwing light on the question of whether carbon can exist in the pyrosphere of the earth as carbon monoxide, the author has re-examined the action of heat on carbon monoxide alone.

According to Deville (1864), carbon monoxide is partly dissociated at a bright red heat into carbon dioxide and carbon, whereas Berthelot (1891), and also Lothian Bell (1891), found that, although carbon dioxide was formed, even at 550°, no trace of carbon deposit could be observed. Berthelot supposed that a volatile carbon suboxide, such as C_2O, was produced. The author shows that carbon monoxide, as prepared by Berthelot from its compound with cuprous chloride, yields, not only carbon dioxide, but also water on heating at 820° and 1250°. Berthelot's monoxide therefore contained hydrogen, and the carbon unaccounted for in his experiments was probably in the form of a hydrocarbon. No suboxide of carbon of the kind which might produce oxalic acid, glycollic acid, or glyoxal could be detected. Deville's observations of the deposition of carbon could be repeated when traces of organic matter or ferric oxide were present. The author draws the conclusion that pure carbon monoxide is not appreciably dissociated at the melting point of lava under normal pressure. R. J. C.

Action of Ozone on Carbon Monoxide. PAUL CLAUSMANN (*Compt. rend.*, 1910, **150**, 1332—1333. Compare Berthelot, *Compt. rend.*, 1879, **88**, 50).—Remsen and Southworth (*Ber.*, 1875, **8**, 1414) were unable to detect the formation of carbon dioxide when ozone acts on carbon monoxide in sunlight; by passing the mixed gases through a solution of barium hydroxide, however, an abundant precipitate of barium carbonate is produced. The oxidation of carbon monoxide by ozone takes place in darkness, but more rapidly in daylight. Traces of water-vapour accelerate the reaction. W. O. W.

Preparation of Pure Argon and Nitrogen. FRANZ FISCHER and OTTO HÄHNEL (*Ber.*, 1910, **43**, 1435—1442).—A special apparatus is described for the purification of crude argon (obtained by the action of calcium carbide on air: Abstr., 1908, ii, 688) from gases other than those of the argon group. With the exception of two iron tubes, containing calcium and copper oxide respectively, and heated in furnaces, the apparatus is made entirely of glass, all joints being fused together. Special stopcocks and stoppers with mercury seals are used, and also a special arrangement for connecting the glass parts with the iron tubes, so that no air can penetrate into the apparatus from the outside. The gas is kept automatically circulating round the apparatus, nitrogen being absorbed by the calcium, and hydrogen and carbon monoxide oxidised by the copper oxide; there are the usual absorbents for moisture and carbon monoxide.

The apparatus may also be used for purifying nitrogen, the calcium being then replaced by copper turnings.

The density of crude argon, purified in the above apparatus was 19·945, agreeing with the value (19·940) obtained by Ramsay and Travers; that of nitrogen was 14·018.

During the circulation of the argon, intensive phosphorescent effects were noticed, being the more pronounced the purer the argon. No such effects were observed in the case of nitrogen. T. S. P.

New Experiments on the Combining Capacity of Argon. FRANZ FISCHER and FRITZ SCHRÖTER (*Ber.*, 1910, **43**, 1442—1454).—The apparatus used by Fischer and Iliovici (Abstr., 1908, ii, 1034;

1909, ii, 139, 232) for the production of an arc in liquid argon has been improved so that it is perfectly gas-tight; it retained the highest vacuum for forty-eight hours, and after working with it for a year the argon used remained quite pure. Special arrangements were also devised for regulating the distance apart of the electrodes, for undercooling the liquid air used to condense the argon in such a way that fractional distillation of the nitrogen did not take place, and for maintaining an arc between metals which either did not disintegrate or only disintegrated with difficulty.

Experiments were carried out with forty-five metals, using argon purified according to the method described in the previous abstract. Some of the metals disintegrated with the formation of a black powder (see succeeding abstract), but the majority did not disintegrate. With the exception of Groups I and VII of the Periodic Table, the metals which did not disintegrate are contained in the left-hand column (sub-group) of each group, the metals in the first two horizontal rows being counted as belonging to the left-hand column. The metals which disintegrated are those in the right-hand column. None of the metals of the platinum and iron groups disintegrated, those investigated being iron, cobalt, nickel, palladium, iridium, and platinum.

When the metal did not disintegrate, the arc formed consisted of incandescent argon, and had a very high resistance; it was also rich in ultra-violet rays. T. S. P.

Modifications of Metals Resulting from Electrical Disintegration in Liquid Argon. Franz Fischer and Fritz Schröter (*Ber.*, 1910, 43, 1454—1464).—When an arc discharge takes place between metal electrodes in pure liquid argon, compounds with argon are not formed. In no case could it be proved that they have a momentary existence, even at the temperature of liquid air. If it does so happen that they exist, they must be far more explosive than cadmium nitride.

Owing to the disintegration, a number of metals were obtained in a new form. Lithium and sodium were obtained as brown, and potassium, rubidium, and cæsium as blue, relatively stable powders. The lithium powder had a density approximately the same as that of liquid argon ($D = 1{\cdot}2$); at 20° lithium has $D = 0{\cdot}534$, so that the density increases enormously when the temperature falls to $-186°$. Zinc and cadmium gave deep black modifications, which were only stable at the temperature of liquid air. Mercury gave a black powder which dissolved in the excess of mercury when the temperature rose.

Copper did not disintegrate, silver only to a very slight extent, and gold slightly more than silver. The disintegrated gold was dark brown by reflected, and green by transmitted light.

Zinc, tin, indium, and manganese gave pyrophoric powders. Bismuth gave a deep black powder, which gradually became grey, and at the same time more dense at room temperature, denoting a change from the amorphous to the crystalline form. Arsenic and antimony gave black powders which did not contain any of the yellow modifications,

although the experiments were carried out under exclusion of daylight.

None of the finely divided powders obtained absorbed argon at room temperature; in the case of zinc, adsorption did not occur even at the temperature of liquid air. This is in marked contrast with the behaviour of finely divided charcoal. T. S. P.

The Liberation of Helium from Minerals by the Action of Heat. D. ORSON WOOD (*Proc. Roy. Soc.*, 1910, *A*, **84**, 70—78).—The minerals were heated in Jena glass tubes (up to 750°) and in quartz tubes (up to 1200°), and the total volume of helium liberated was measured. For monazite very little of the helium came off when the temperature was maintained at 500°, but above this temperature the evolution was more rapid, although even at 720° it did not reach a limit after very prolonged heating. At 900° to 1200° the greater part of the helium present came off in the first day. For thorianite a practical limit could be reached at each temperature, and was found to be 0·7% at 300° after five hours, 8·5% at 500° after eighty hours, 62·3% at 750° after three hundred and twenty hours, and the whole at 1000° after thirty hours. The laws governing the liberation of gas agree with the view that a small proportion of the gas exists diffused through the mineral, and that most of it is concentrated in minute cavities within it. The pressure of helium in a thorianite crystal at 0° must be very great, possibly above 200 atmospheres.

F. S.

Crystallography of Some Inorganic Compounds. FERRUCCIO ZAMBONINI (*Zeitsch. Kryst. Min.*, 1910, **47**, 620—629).—Details respecting the following salts are given. Potassium thiostannate, $K_2SnS_3,3H_2O$ (cubic, D^{18} 1·847). Potassium iridium oxalate,

$$K_3Ir(C_2O_4)_3,4H_2O$$

(triclinic, $a:b:c=0·7319:1:0·9565$; $\alpha=88°34\frac{1}{2}'$, $\beta=94°30'$, $\gamma=57°1'$. D^{19} 2·510). Silver iridium oxalate, $Ag_3Ir(C_2O_4)_3,3H_2O$ (monoclinic, $a:b:c=1·2760:1:0·8345$; $\beta=114°43'$). Copper dichromate, $CuCr_2O_7$,1 or $2H_2O$ (triclinic, $a:b:c=0·6133:1:0·5117$; $\alpha=67°2'$, $\beta=125°14'$, $\gamma=111°26'$. D^{19} 2·286). Tetramethylammoniumiron nitrosulphide, $[Fe_4(NO)_7S_3]NMe_4$ (triclinic, $a:b:c=0·8648:1:1·3125$; $\alpha=87°29\frac{1}{2}'$, $\beta=106°7'$, $\gamma=93°44'$. D^{19} 2·056). Tetraethylammoniumiron nitrosulphide, $[Fe_4(NO)_7S_3]NEt_4$ (triclinic, $a:b:c=1·0221:1:1·0247$; $\alpha=85°8'$, $\beta=97°8'$, $\gamma=99°17\frac{1}{2}'$. D^{19} 1·883). Glucinum sulphate, $GlSO_4,6H_2O$ (cubic). L. J. S.

The Behaviour of Lithium towards Sodium, Potassium, Tin, Cadmium, and Magnesium. G. MASING and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1910, **67**, 183—199).—The alloys are melted in quantities of only one or two grams in Jena glass tubes, or, for high temperatures, in iron tubes, in an atmosphere of hydrogen, which does not react rapidly with lithium below 400°. The thermocouple is of fine wires, protected by a capillary of Jena glass.

Lithium melts at 179°. It is only very slightly miscible at its melting point with sodium or potassium. Glass is wetted by molten lithium, but not by sodium, so that the boundary between the two

metals is a meniscus. Lithium and tin form three compounds: Li_4Sn, forming a maximum on the freezing-point curve at 680°; Li_3Sn_2, forming a flat maximum at 465°; and Li_2Sn_5, reacting with the melt at 320°. The freezing-point curve of alloys of lithium and cadmium has a maximum at 541°, corresponding with the compound LiCd, and a break at 505°, indicating a possible compound, $LiCd_2$. Lithium and magnesium appear to form solid solutions, but at the temperature of fusion the alloys attack the glass sheath of the thermocouple. The elements of the alkali and zinc groups are compared with respect to their power of forming compounds. C. H. D.

The Electrolytic Preparation of Rubidium. GEORG VON HEVESY (*Zeitsch. anorg. Chem.*, 1910, **67**, 242—247).—Rubidium is the only alkali metal that has not hitherto been prepared electrolytically. Rubidium hydroxide (100 grams) is melted in a nickel vessel, and the iron cathode wire and iron anode cylinder are surrounded by magnesite cylinders. The cathode cylinder is closed above, except for a small opening for the escape of the hydrogen which is formed at first. After a few minutes, this opening is closed with magnesite. The nickel vessel is rapidly cooled after the electrolysis, the mass of hydroxide is broken, and the cylinder containing the rubidium is opened under pyridine cooled by a freezing mixture. The yield is 30% after three-quarters of an hour, using a current of 5 amperes. Part of the loss is due to the readiness with which oxygen is absorbed by the hydroxide, and thus conveyed to the cathode. The solubility of rubidium in its hydroxide is only small, but the reaction $RbOH + Rb = Rb_2O + \frac{1}{2}H_2$ is perceptible at 360°. The absorption of heat in this reaction decreases in the series Na–K–Rb–Cs.

Rubidium hydroxide has D^{11} 3·203, and m. p. 301° ± 1°.

Alloys of rubidium with potassium and sodium are obtained by the action of these metals on rubidium hydroxide. C. H. D.

Some Complex Metallic Cations. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **67**, 248—249).—If a solution of a silver salt is run into a solution of ammonia, the point at which a permanent precipitate is produced is readily observed, and the formula of the complex cation may be deduced. The formulæ $Ag(NH_3)_2$, $Ag(NH_2Me)_2$, and $Ag(NH_2Et)_2$ are thus obtained, in agreement with the results of other methods. When copper sulphate and ammonia are employed, the end-point is less sharp, but the titrations indicate the formula $Cu(NH_3)_4$. Sharp results are not obtained with zinc, cadmium, or nickel. C. H. D.

Nature of Schaum's Substance *B*. A. P. H. TRIVELLI (*Chem. Weekblad*, 1910, **7**, 381—387. Compare Schaum, *Zeitsch. Elektrochem.*, 1908, **14**, 483).—Schaum's substance *B* is a silver halide which is more soluble than the corresponding silver halide which has not been exposed to light. It, and not the original silver halide, is the starting point of the author's series of photochemical decompositions.

A. J. W.

The Solubility of Sparingly Soluble Silver Salts. G. STAFFORD WHITBY (*Zeitsch. anorg. Chem.*, 1910, 67, 107—109).—The solubility of very sparingly soluble silver salts has hitherto been determined by physical methods. The analytical method described by the author (this vol., ii, 654) enables a chemical determination to be made. The solubilities of the arsenate, arsenite, bromate, chloride, chromate, ferricyanide, iodate, oxalate, oxide, and thiocyanate are given. A litre of water dissolves 0·00154 gram of silver chloride at 21°, but 0·0217 gram at 100°; the precipitate should therefore not be washed with boiling water in accurate work. One % of hydrochloric acid diminishes the solubility of silver chloride, but further additions increase it, so that the solubility in 5% hydrochloric acid is greater than in water. The solubility of silver chromate does not diminish with rising temperature, as supposed by Abegg and Cox (Abstr., 1904, ii, 256). The solubility of the oxide increases with time, only becoming constant after fourteen days. C. H. D.

Colloidal State of Calcium Carbonate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 266).—Chalk (containing calcium sulphate) was washed by decantation during eleven days. When the washed calcium carbonate was filtered from the last wash-water, it was always observed that the filtrate was slightly turbid. If, however, this liquid, after ten minutes, was re-filtered, a clear filtrate was obtained. The conclusion is drawn that calcium carbonate can exist in the colloidal state, although for only a short time.

E. H.

Action of Alkali Nitrates on Strontium Carbonate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 162—164).—It has been shown previously (this vol., ii, 411) that under certain conditions calcium or barium, but not strontium, carbonate is attacked by boiling sodium nitrate solution. It is found, however, that a small amount of strontium nitrate is formed when a mixture of strontium carbonate (1 part) and sodium nitrate (2—3 parts) is either heated gradually to redness and kept at this temperature for ten minutes, or heated at 325° for twenty minutes. Moreover, if a solution of potassium nitrate (75 grams) in water (100 c.c.), containing strontium carbonate (10 grams), is heated on a water-bath for thirty-two hours, the filtrate is found to contain a small, although quite definite, amount of strontium in solution. E. H.

Barium Sulphate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 267).—Barium sulphate was precipitated from very dilute solutions in two tubes. One of the latter was kept in comparative darkness, the other was exposed to sunlight during several hours per day for fourteen months. The barium sulphate exposed to sunlight polymerised slightly more rapidly, and formed a granular precipitate. In the unexposed tube the particles of barium sulphate forming the precipitate were appreciably smaller than the others.

E. H.

The Reversible Action of Oxygen on Magnesium Chloride. WILHELM HIRSCHKIND (*Zeitsch. anorg. Chem.*, 1910, 67, 113—148).—The equilibrium between oxygen and magnesium chloride, or between chlorine and magnesium oxide, has been investigated by Haber and Fleischmann, and by Moldenhauer (Abstr., 1907, ii, 84, 85). Their experiments have now been repeated with increased precautions.

Passing the gas over the heated solid and analysing the issuing gases, it is found that when chlorine acts on magnesium oxide or on a mixture of equal parts of oxide and chloride, the correct value for the equilibrium is obtained. From the other side, a mixture of chlorine and oxygen, containing only slightly less than the equilibrium proportion of chlorine, gives a nearly correct value when passed over the mixed solids, but when a mixture richer in oxygen is used, the evolution of chlorine is always low. It is uncertain whether this difference is due to the formation of an oxychloride.

A second apparatus is described for making statical experiments, the solid being left in contact with a prepared mixture of gases for a given time at a given temperature. It is found that whilst the equilibrium is attainable from both sides, the prolonged passage of gas leads to a new apparent equilibrium, corresponding with a much lower pressure of chlorine. This effect appears to be due to the formation of an oxychloride, and there is also evidence for the absorption of chlorine by finely divided magnesium oxide.

The values of $k_p = p_{Cl_2}/p_{O_2}^{\frac{1}{2}}$ found are: by the statical method, at 621°, 2·53; at 665°, 2·97; and at 714°, 3·4. The value obtainable from both sides by the dynamical method is, at 665°, 3·18. The heat developed by the reaction $MgCl_2 + \frac{1}{2}O_2 = MgO + Cl_2$ is about 6000 cal., within the range investigated. The calculation of the theoretical value is uncertain, as the specific heats of the reacting solids at different temperatures are unknown. C. H. D.

Crystalline Form and Composition of the Hydrated Magnesium Carbonate prepared by Moressée. Its Relation to Landsfordite. GUISEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1910, 234—265).—Moressée has shown (*Ann. Soc. géol. Belg.*, 37, 151—156) that when the mixture of calcium and magnesium oxides, obtained by calcining dolomite, is powdered, suspended in water at 10°, and the liquid saturated with carbon dioxide under a pressure of 5—6 atmospheres, only the magnesium oxide is dissolved. The filtrate deposits crystals, the composition of which is found by the author to correspond with $MgCO_3,5H_2O$, although in some cases a somewhat higher percentage of magnesia is found, probably owing to partial decomposition.

The crystals obtained by Moressée are monoclinic [$a:b:c$ = 1·6323 : 1 : 0·96676, $\beta = 77°50'58''$], the general form being an hexagonal prism. The three principal birefringences are $n_g - n_p$ 51, $n_g - n_m$ 38, $n_m - n_p$ 13. The crystals are harder than gypsum, but softer than Iceland spar; they have D^{19} 1·73. The crystalline form is practically identical with that of landsfordite. It is suggested that Moressée's carbonate is identical with the latter mineral, the smaller proportion of carbon dioxide (Dana gives $4MgO,3CO_2,22H_2O$ as

representing the composition of landsfordite) being due to decomposition on analysis.

Moressée's carbonate is soluble in 267 parts of cold water, the solution being alkaline to both litmus and phenolphthalein. The residue obtained by the spontaneous evaporation of its aqueous solution seems to contain both the original substance and a small quantity of nesquéhonite, $MgCO_3,3H_2O$. A solution of Moressée's carbonate becomes turbid when heated to boiling, but the precipitate redissolves on cooling the liquid to 10°, and the latter, when evaporated, leaves an amorphous residue containing crystals of both $MgCO_3,5H_2O$ and of nesquéhonite.

When the solution of magnesia obtained technically by Moressée is boiled, a precipitate is formed having the composition corresponding with $4MgO,3CO_2,14{\cdot}6H_2O$, but if heated at 40—50° on a water-bath, a crystalline deposit of rectangular needles is produced, which contains nesquéhonite, but no trace of the pentahydrated carbonate.

E. H.

Oxychlorides of Zinc. DRIOT (*Compt. rend.*, 1910, **150**, 1426—1428. Compare Schindler, *Ann. Mag. Pharm.*, 1831, **36**, 45; Kane, *Ann. Chim. Phys.*, 1839, [ii], **2**, 72; Mailhe, Abstr., 1901, i, 601).—Determinations of the solubility of zinc oxide in an aqueous solution of zinc chloride indicate the existence of two oxychlorides having the composition $ZnCl_2,4ZnO,6H_2O$, and $ZnCl_2,ZnO,1{\cdot}5H_2O$. These have been isolated and analysed. The first is amorphous and loses $5H_2O$ at 200°, whilst the latter forms microscopic crystals, losing $1H_2O$ at 230°, and decomposing at a higher temperature. A study of the equilibrium in systems containing these oxychlorides with zinc chloride in aqueous solution has shown that the composition of these substances does not vary with temperature. No evidence has been obtained for the existence of eight oxychlorides described by previous observers.

W. O. W.

Zinc Hydrazide and a General Method for the Preparation of Metal Hydrazides. ERICH EBLER and R. L. KRAUSE (*Ber.*, 1910, **43**, 1690—1695. Compare Abstr., 1909, ii, 234).—When hydrazine and zinc ethyl dissolved in dry ether interact, a colourless precipitate is formed, which ignites spontaneously when it comes in contact with the air. This has approximately the composition ZnN_2H_2. The same zinc hydrazide is formed from zinc diamide, $Zn(NH_2)_2$, and anhydrous hydrazine in ethereal suspension. The anhydrous diamides of other metals react with hydrazine in a similar manner, forming hydrazides which ignite spontaneously in the air.

E. F. A.

A Supposed Allotrope of Lead. ERNST COHEN and KATSUJI INOUYE (*Chem. Weekblad,* 1910, **7**, 454—458. Compare Lehmann, Abstr., 1890, 437).—Measurements of the *E.M.F.* between the forms of lead obtained by Lehmann by the electrolysis under certain conditions of solutions of lead salts have proved that these forms are not allotropic modifications of lead, but are identical.

A. J. W.

Analysis of Some Bolivian Bronzes. MORRIS LOEB and S. R. MOREY (*J. Amer. Chem. Soc.*, 1910, **32**, 652—653).—Analyses are given

of six specimens of various native bronze implements: (1) copper 91·81, tin 7·56; (2) copper 90·51, tin 8·92; (3) copper 95·59, tin 4·48; (4) copper 97·43, arsenic 2·14; (5) copper 94·96, tin 4·98, sulphur 0·53; (6) copper 91·43, tin 7·05.

Approximate densities: (1) 8·68, (2) 8·94, (3) 8·92, (4) 8·89, (5) 8·61, (6) 8·18(?).

The complete absence of silver points to the tin being obtained from casserite rather than native tin. L. DE K.

Preparation of Mercuric Chloride from Mercuric Sulphate and Sodium Chloride by the Wet Process. ERWIN RUPP and W. KLEE (*Apoth. Zeit.*, 1910, No. 26. Reprint, 3 pp.).—One hundred parts of mercuric sulphate are mixed with 40 parts of common salt, well powdered, and then moistened with 20 parts of 5% hydrochloric acid. The mass is frequently stirred, and, after twenty-four hours, extracted with 95% alcohol in a suitable extraction apparatus. The alcohol is recovered by distillation, and the product recrystallised from boiling water. The yield is about 90%.

Mercuric nitrate solution should be converted into chloride by addition of a sufficiency of sodium chloride, and then carefully neutralised if it is desired to precipitate the mercury as sulphide. L. DE K.

Nitrides and Oxides from Aluminium Heated in Air. J. O. SERPEK (*Compt. rend.*, 1910, **150**, 1520—1521. Compare Kohn-Abrest, this vol., ii, 506).—Some of the observations made by Kohn-Abrest had already been recorded (Fichter, Abstr., 1907, ii, 691; Bronnert, *Bull. Soc. Ind. Mulhouse*, 1909). The author has been unable to obtain a nitride differing from AlN in composition, as described by Kohn-Abrest. W. O. W.

Adsorptive Power of Hydroxides of Silicon, Aluminium, and Iron. IV. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1910, **67**, 110—112; *Biochem. Zeitsch.*, 1910, **25**, 420—424. Compare this vol., ii, 104).—Talc and steatite, like clay, have the power of adsorbing colloids (soap, starch, dextrin) and complex dyes, such as aurin, fluorescein, and cochineal, whilst acids and salts are not adsorbed. C. H. D.

Formation of Basic Aluminium Sulphate when Zinc Sulphate is Boiled with Alum. O. SCHWEISSINGER (*Pharm. Zentr.-h.*, 1910, **51**, 493—494).—When a solution of 75 grams of zinc sulphate and 75 grams of alum in 1000 grams of water is boiled, a precipitate of basic aluminium sulphate begins to form after about ten minutes. Under the same conditions, a solution of aluminium sulphate gives no precipitate. Magnesium sulphate acts similarly to zinc sulphate; sodium or potassium sulphate has no effect. T. S. P.

Reactions of Artificial Zeolites. ANTONY G. DOROSCHEWSKY and A. BARDT (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 435—442).—The

authors have investigated the influence of various conditions on the velocity with which an artificial sodium zeolite is attacked by salt solutions: $Na_2O,Al_2O_3,nSiO_2 + RSO_4 = RO,Al_2O_3,nSiO_2 + Na_2SO_4$. The zeolite employed had the percentage composition: SiO_2, 42·06; Al_2O_3, 20·45; Na_2O, 12·10, and H_2O, 25·00, and was sieved so as to render it approximately uniform in size of grain.

The zeolite is attacked considerably more readily by an aqueous solution of calcium chloride containing an amount of calcium equivalent to the sodium of the zeolite than by a solution of similar concentration in 65% aqueous alcohol. That this variation in the velocity of the reaction is due to a difference in the extent to which the calcium chloride is dissociated in the two solutions is confirmed by the observation that the zeolite is not acted on by an aqueous solution of mercuric cyanide. In this action, the velocity is at first very great, but later gradually diminishes, a condition of equilibrium being attained only after a very considerable period of time. Rise of temperature is accompanied by marked increase in the rate of change, but the character of the velocity curve remains unaltered. Experiments with solutions of magnesium, calcium, strontium, and barium chlorides show that increase in the atomic weight of the metallic ion of the attacking salt results in increased velocity of the reaction; with magnesium chloride the action is very considerably slower than with the other three chlorides. T. H. P.

Production of Cementation Steel. VI. FEDERICO GIOLITTI and F. CARNEVALI (*Atti. R. Accad. Sci. Torino*, 1910, **45**, 376—387).—The authors have already given the results of experiments in which steels with low carbon contents (0·05—0·10%) were subjected to the carburising action of various gases (Abstr., 1909, ii, 240). The same method of experimenting has now been applied to two samples of steel containing (*A*) 0·18% C, 0·35% Mn, 0·05% Si, 0·07% P, and 0·05% S, and (*B*) 0·94% C, 0·90% Mn, 0·17% Si, 0·04% P, and 0·02% S. At 800° cementation is less intense for steel *B* than for the soft steel, support thus being given to the view that a considerable part is played by the phenomena of diffusion of the carbon owing to differences of concentration among the different portions of the mass of β or γ iron in which it is dissolved. When ethylene or methane is employed at either the ordinary or reduced (600 or 450 mm.) pressure, the hyper-eutectic zone is considerably deeper in steel *B* than in *A*. At 900° the second factor in the cementation process, that is, the diffusion of the carburising gas into the metallic mass, begins to play a preponderating part, and this is still more the case when carbon monoxide is employed; similar results are observed with illuminating gas rich in carbon monoxide, and, to a more marked extent, at a temperature of 1000°. At 1100° the differences in the course of the carburisation, due to the different initial concentrations of the carbon, are more distinct than at lower temperatures. Microphotographs render evident the accumulation of the cementite in the zone contiguous with the superficial eutectic stratum. T. H. P.

The Ternary System Iron–Copper–Nickel. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1910, **67**, 1—16).—Iron and copper form two

limited series of solid solutions (Sahmen, Abstr., 1908, ii, 187), whilst nickel forms continuous series of solid solutions with both iron and copper (Guertler and Tammann, Abstr., 1905, ii, 528; 1907, ii, 174); thus the addition of nickel may be expected to reduce the gap in the mutual solubilities of iron and copper in the solid state. The limits are more readily determined by microscopical than by thermal methods, as the diffusion is slow in comparison with the rate of cooling, and it is therefore necessary to anneal for a long time after freezing in order to obtain equilibrium. The results are expressed in the form of a triangular diagram and of several vertical sections through the space-model.

The limit of saturation of the ternary solid solutions is a curve starting from 96·5% Fe and 3·5% Cu, cutting the nickel diagonal at 40% Ni, and ending at 2·75% Fe and 97·25% Cu. All alloys falling outside this curve are homogeneous if sufficiently annealed. The alloy containing 72% Fe, 7% Cu, and 24% Ni has when etched with nitric acid a structure resembling that of martensite.

The unsaturated solid solutions of medium composition are exceedingly tough, the crystals being capable of great deformation without breaking. All the alloys are magnetic at the ordinary temperature. C. H. D.

Ultra-microscopical Studies. III. A Photo-chemical Reaction. J. AMANN (*Chem. Zentr.*, 1910, i, 1117; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 4—8, 24—28. Compare Abstr., 1909, ii, 983, 1056).—The sensitiveness of certain alkali-iron salts of organic acids may be due, in different cases, to (1) simple decomposition of the double salt and reduction of ferric to ferrous iron (ferric ammonium oxalate); (2) reduction, accompanied by coagulation of the colloid and formation of a gel, the reaction being reversed in darkness (ferric potassium tartrate and ferric sodium pyrophosphate with sodium or ammonium citrate); (3) reduction of the iron and oxidation of the organic radicle, without the formation of a gel. The last case has not been observed. Only those double ferric salts are sensitive to light which contain a reducing group, principally HCOH. Substances which accelerate the coagulation retard the re-formation of a sol. The action of light on the colloidal complex is believed to be a hydrolysis, forming ferric hydroxide and the organic acid, followed by reduction of the ferric iron. C. H. D.

Colloidal Character of the Chromopolysulphuric Acids. PABLO MARTÍNEZ-STRONG (*Compt. rend.*, 1910, **150**, 1172—1174; *Anal. Fis. Quim.*, 1910, **8**, 199—202).—It is suggested that Recoura's chromopolysulphuric acids are negative colloids, since they are precipitated by almost all metallic salts, by acids, and by heat, but not by ammonia, and the precipitate appears to be the same in every case.

Examination of the acids with the ultramicroscope confirms this view, numerous brilliant particles being seen with characteristic Brownian motion.

After precipitation, 3, 4, or 5 molecules of sulphuric acid remain in

solution, and the precipitate has the composition $H_2Cr_2(SO_4)_4$ (sulphochromic hydrate). It is uncertain whether the sulphuric acid is uncombined in the solid chromo-acids or is liberated when they are dissolved, or is only set free on precipitation by the salts, etc. Sulphochromic hydrate is obtained on heating either tetra-, penta-, or hexasulphochromic acids at 140—150°.

The author, adopting Duclaux's hypothesis of colloids (this vol., ii, 108), suggests that the sulphochromic hydrate constitutes the nucleus or micella of the colloid round which the remaining molecules of sulphuric acid are loosely aggregated in the intermicellary liquid.

The crystallisation of chromium sulphate in the violet form in presence of sulphuric acid is attributed to the hydrolating action of the latter. R. J. C.

Metallurgy of Uranium and Vanadium. JUSTIN H. HAYNES (*Mines and Minerals*, 1909, 30, No. 3, 139—140).—The discovery of the mineral carnotite in West Colorado furnished the first example of the occurrence together of uranium and vanadium in workable quantities. At first the uranium only was extracted, but as the demand for vanadium increased, the problem of how to separate the two had to be considered. A recent method is founded on the fact that both the uranium and vanadium in carnotite are readily soluble in hot sodium carbonate, forming sodium uranium carbonate ($2Na_2CO_3,UO_2,CO_3$) and sodium vanadate (Na_3VO_4), thus separating them from calcium and iron. The uranium is then precipitated as sodium uranate ($Na_2O,3UO_3$) with sodium hydroxide, and the vanadium subsequently separated from the filtrate as calcium vanadate [$Ca_2(VO_3)_2$]; another modification was the formation of ferrous vanadate without the employment of lime, but it presented serious practical difficulties owing to the large quantity of colloidal slime which was formed.

In 1908, Fleck and Haldane patented a method in which the crushed ore is agitated with 15—20% sulphuric acid, and the acid solution containing the uranium, vanadium, iron, and copper brought into contact with fresh ore until neutral, when some of the required constituents will be precipitated upon it as basic sulphates or carbonates; the enriched ore is then treated with fresh acid, and the neutral solutions clarified by filtration; powdered limestone added until the uranium, vanadium, and copper fractions just commence to separate; the solution is then freed from calcium sulphate, and the required fraction completely precipitated by further treatment with limestone. The product (a complex mixture) may be dried, ignited, or else further purified by any of the known methods.

The author considers it improbable that any method involving the employment of sulphuric acid can be commercially successful.

F. M. G. M.

Fluorine Salts of Vanadium. N. COSTĂCHESCU (*Ann. Sci. Univ. Jassy*, 1910, 6, 117—123).—Ephraim (Abstr., 1903, ii, 418) has put forward the rule that in the series of complex salts formed from vanadium fluoride and the fluorides of the alkali metals, including ammonium, the greater the atomic weight of the alkali metal the

smaller is the number of molecules of the alkali fluoride contained in the salt. The author finds that this rule holds for the rubidium and cæsium compounds, which, together with the potassium compound, are of the type $\left[V\genfrac{}{}{0pt}{}{F_4}{2H_2O}\right]M$, containing only one molecule of the alkali fluoride. The alkali metal can be replaced by aniline, and the compounds still conform to this rule, since the salts then formed are $[VF_6](NH_3Ph)_3$ and $\left[V\genfrac{}{}{0pt}{}{F_5}{H_2O}\right](NH_3Ph)_2$.

The salt $[VF_6](NH_3Ph)_3$, is formed by the crystallisation of a concentrated solution of vanadium trifluoride (1 mol.) in excess of aniline hydrofluoride (3 mols.); pale green crystals. The compound $\left[V\genfrac{}{}{0pt}{}{F_5}{H_2O}\right](NH_3Ph)_2$ results when 2 mols. of aniline hydrofluoride are used to 1 mol. of vanadium fluoride; green crystals.

The salts $\left[V\genfrac{}{}{0pt}{}{F_4}{2H_2O}\right]M$, where M is either K, Rb, or Cs, are each obtained by mixing solutions of vanadium trifluoride and of the alkali fluoride in the proper proportions (1 mol. : 1 mol.) and evaporating if necessary. T. S. P.

Electrolytic Refining of Bismuth. FRITZ FOERSTER and E. SCHWABE (*Zeitsch. Elektrochem.*, 1910, **16**, 279—281).—In the electrolytic refining of lead, the anode mud contains bismuth, lead, and silver. It is found that this mixture can be separated electrolytically, using a solution of bismuth silicofluoride as electrolyte; the lead passes into solution, and silver remains undissolved. The potentials of lead and bismuth in solutions of their silicofluorides containing one equivalent per litre are $+0·144$ and $-0·295$ volt respectively (compared with the hydrogen electrode). Solutions containing as little as 26 grams of bismuth per litre give perfect deposits with 0·004 ampere per sq. cm. Stronger solutions and higher temperatures allow higher current densities to be used. T. E.

Halides of Tantalum. WALTER K. VAN HAAGEN (*J. Amer. Chem. Soc.*, 1910, **32**, 729—731).—Tantalic bromide, $TaBr_5$ (Rose, *Ann. Phys. Chem.*, 1856, [ii], **99**, 87), can be prepared by passing bromine vapour over a strongly heated mixture of freshly ignited tantalic oxide and pure sugar-carbon, air having been previously removed by heating the mixture in a current of dry carbon dioxide. The salt crystallises in long, yellow plates, has m. p. about 240° and b. p. about 320°, can be sublimed in an atmosphere of hydrogen, fumes in moist air, and reacts readily with methyl or ethyl alcohol.

Neither Rose (*loc. cit.*) nor Moissan (Abstr., 1902, ii, 266) was able to obtain a tantalum iodide, but it has now been found that *tantalic iodide*, TaI_5, can be prepared by heating the bromide in a current of hydrogen iodide; it sublimes in nearly black plates, melts to a dark brown liquid, can be distilled in a current of carbon dioxide, and fumes in moist air. E. G.

Tantalum Sulphide. HEINRICH BILTZ and CARL KIRCHER (*Ber.*, 1910, **43**, 1636—1645).—Tantalum sulphide has hitherto not been

prepared in a pure condition, so that the formula TaS_2, which does not correspond with that of the oxide, Ta_2O_5, was doubtful. The author prepares the pure sulphide by passing a dry mixture of hydrogen sulphide and carbon disulphide over heated tantalum oxide. The oxide is attacked at 650°, but the pure sulphide is best obtained at temperatures higher than 900°. It is stable at all events up to 1300°, and above 1200° it begins to change from the amorphous to the crystalline condition. The formula was found to be TaS_2, the analysis being carried out by burning the sulphide in a stream of oxygen, weighing the tantalum oxide left, and estimating the sulphur dioxide produced as barium sulphate.

Tantalum oxide is not appreciably acted on by hydrogen sulphide, even at 1200°. T. S. P.

Formation of Colloidal Gold Solutions by the Auto-oxidation of Aurous Chloride. LUDWIG VANINO and L. RÖSSLER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 289—290).—When aurous chloride, prepared by heating the auric salt at 200°, is acted on by hot water, a blue colloidal solution of gold is at once obtained. With a large quantity of water, the blue colour is not evident until after about twelve hours; at the same time a gold mirror appears on the surface of the solution. On addition of sodium chloride, the blue colour changes to a reddish tint; potassium hydroxide has no effect on the colour. The production of the colloidal gold is attributed to the change: $3AuCl = AuCl_3 + 2Au$. H. M. D.

Preparation of Colloidal Metals by means of Acraldehyde. NICOLA CASTORO (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 283—289).—Colloidal solutions of gold, platinum, osmium, palladium, ruthenium, iridium, rhodium, and silver are very readily obtained when dilute solutions of salts of these metals are treated with a small quantity of a 33% solution of acraldehyde. The hydrosols obtained in this way are more stable than those formed by reduction with formaldehyde or by the electrical method. The reducing action of the acraldehyde is supposed to be due, not only to the aldehyde group, but also to the double linking. In support of this view it has been found that metallic hydrosols can also be obtained by the action of allyl alcohol. Acid solutions of gold chloride are reduced by allyl alcohol with the production of bright red gold hydrosols. Acraldehyde has no action in acid solutions, and these must first be made neutral or slightly alkaline by addition of potassium carbonate. H. M. D.

Mineralogical Chemistry.

Samsonite, a Manganiferous Silver Mineral from the Harz. WERNER and FRAATZ (*Centr. Min.*, 1910, 331—336).—This new mineral was found in the Samson mine at St. Andreasberg, in association with pyrargyrite, galena, pyrolusite, quartz, calcite,

apophyllite, etc. The monoclinic crystals resemble miargyrite in appearance; they are steel-grey, but red by transmitted light. Analysis gives the formula $2Ag_2S,MnS,Sb_2S_3$, which is similar to that of pyrargyrite with part of the silver replaced by manganese.

S.	Ag.	Sb.	Mn.	Cu.	Fe.	$CaCO_3$.	$MgCO_3$.	SiO_2,Pb,As.	Total.
20·55	45·95	26·33	5·86	0·18	0·22	0·41	0·46	traces	99·86

The associated greyish-black calcite and rose-red apophyllite owe their colour to the presence of some manganese and iron.

L. J. S.

Action of Acetic Acid on Clays (Kaolin and Allophane). RUDOLF VAN DER LEEDEN (*Centr. Min.*, 1910, 289—295).—Comparative experiments were made with kaolin (anal. I) from Zettlitz, near Carlsbad, Bohemia, and allophane (anal. II) from Ohio. Analysis I corresponds with the ratio $Al_2O_3:SiO_2 = 1:2$, and anal. II with $1:0·756$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alkalis.	Loss on ignition.	Total.
I.	47·30	41·70	0·20	0·85	0·49	2·06	7·54	100·14
II.	18·47	41·53	0·65	1·62	0·30	0·75	36·85	100·17

These materials were shaken for eight days with 6% or 12% acetic acid. The kaolin was only slightly attacked, about 1—1½% being dissolved, and in the solution $Al_2O_3:SiO_2 = 1:1$. Of the allophane, about 11% was dissolved, and the ratio of $Al_2O_3:SiO_2$ in the solution was the same as in the mineral itself. This chemical difference between kaolin and allophane affords a means of distinguishing these two kinds of clay when optical methods fail. Kaolin has resulted by the gradual alteration of felspar, whereas allophane is a colloidal substance precipitated from solution as a jelly (compare Stremme, Abstr., 1908, ii, 1041).

L. J. S.

Synthesis of Anglesite. GUISEPPE PIOLTI (*Atti R. Accad. Sci. Torino*, 1910, **45**, 373—375).—Immersion of iron pyrites in lead nitrate solution for a period of sixteen and a-half years resulted in the formation on the pyrites of slender needles of anglesite and traces of limonite.

T. H. P.

Composition of Hulsite and Paigeite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], **29**, 543—549).—A re-determination of the boric acid in these supposed new minerals (Abstr., 1908, ii, 507) made by Wherry and Chapin with their new methods (Abstr., 1909, ii, 92) gave in analysis II of hulsite previously quoted the figure 10·44 instead of 25·27%; and in analysis III of paigeite, 9·83 instead of 20·89%. The differences are partly accounted for by the presence of tin, which was overlooked in the original analyses. The following new analyses are given: I, of hulsite free from magnetite, but containing a considerable amount of insoluble gangue; and II and III, of different samples of paigeite, also containing gangue.

	FeO.	MgO.	CaO.	Fe_2O_3.	SnO_2.	B_2O_3.	Insol.	SiO_2.	Al_2O_3.	H_2O, &c.	Total.
I.	27·71	4·29	9·11	15·21	7·07	9·20	18·63		[8·78]		100·00
II.	40·82	2·04	4·13	18·67	3·18	9·10	16·10		[5·96]		100·00
III.	35·02	2·12	8·79	14·90	2·80	6·94	18·57	3·10	2·34	[5·432]	100·00

Doubts still exist as to which constituents, especially the calcium, are to be referred to the minerals themselves and which to the gangue, The "probable" formulæ are given as: for hulsite

$$12(Fe,Mg)O,2Fe_2O_3,SnO_2,3B_2O_3,2H_2O,$$

and for paigeite, $30FeO,5Fe_2O_3,SnO_2,6B_2O_3,5H_2O$, but it is suggested that paigeite may possibly be a mixture of hulsite and an iron borate.

L. J. S.

Mineral with Optical Scroll Structure Contained in Holocrystalline Phosphorites from Quercy. ALFRED LACROIX (*Compt. rend.*, 1910, **150**, 1388—1390).—Quercy phosphorite contains colophanite, α-quercyite and β-quercyite, and a holocrystalline type of mineral. The last constitutes fungoid concretions which are found on the walls of cracks in the phosphorite of Mouillac, and also as nodules in clays of the same formation. Its fracture is flinty, of dead white colour, and shows long, interlocked fibres. Under the microscope, it is seen to have the characteristic scroll structure discovered in calcedonite by Michel Lévy, and imitated by Wallerant in organic compounds by melting them in presence of optically active substances. Analysis shows that the mineral is practically identical with dahllite, of which it is supposed to be a special habit.

The author has observed the same helical structure in dufrenite from Rochefort-en-Terre.

R. J. C.

Physiological Chemistry.

Acapnia and Shock. VI. Acapnia as a Factor in the Dangers of Anæsthesia. YANDELL HENDERSON and MARTIN MCRAE SCARBROUGH (*Amer. J. Physiol.*, 1910, **26**, 260—286).—Anæsthetics prevent shock because they diminish pain-hyperpnœa, and thus obviate the development of acapnia. Respiratory excitement during the induction of anæsthesia diminishes the carbon dioxide of the blood, and thus tends to induce subsequent apnœa which may be fatal. Skilful anæsthesia consists in maintaining the threshold of the respiratory centre for carbon dioxide at a nearly normal level, and in avoiding the development either of acapnia or hypercapnia. Under anæsthesia this threshold may be elevated 50% above normal, or depressed 50% below normal. Such a depression causes vigorous hyperpnœa, which, if long continued, may result in intense acapnia.

W. D. H.

Tonometry of the Gases of the Blood. PIERRE FIRKET (*Bull. Acad. roy. Belg.*, 1910, 287—294).—The author has repeated the experiments of Fredericq (*Centr. Physiol.*, 1893, **7**; 1894, **8**) and of Bohr (Abstr., 1891, 344; 1905, ii, 729), using the apparatus employed

by each of these workers and also the microtonometer devised by Krogh (*Skand. Arch. Physiol.*, 1908, **20**, 259). The results obtained show that the tension of the oxygen in the arterial blood of the dog amounts to 13—14% of an atmosphere, that in the alveoli being 18%. For carbon dioxide the tension (3—4% of an atmosphere) is approximately the same as that in the air of the alveoli. The author considers with Fredericq that diffusion alone governs the gaseous exchanges at the surface of the pulmonary alveoli at the moment of hæmatosis, and that consequently Bohr's secretion hypothesis is untenable. Meanwhile, Krogh (this vol., ii, 512), working in Bohr's laboratory, has obtained similar results, thus confirming Fredericq and the author. E. H.

The Relative Magnitude of the Parts Played by the Proteins and Hydrogen Carbonates in the Maintenance of the Neutrality of Blood. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, **7**, 351—358).—The concentrations of hydrogen ions in 8% solutions of the serum-proteins, dissolved in solutions of known acidity or alkalinity, have been determined with the aid of the gas-chain. In passing from the reaction $0\cdot37 \times 10^{-7} N H^+$ (the reaction of normal blood) to the reaction $1\cdot00 \times 10^{-7} N H^+$ (the reaction seen in marked acid poisoning), 100 c.c. of an 8% solution of the serum-proteins at 34° neutralises the equivalent of 22·5 c.c. of $N/100$-hydrochloric acid. According to L. J. Henderson, the hydrogen carbonates in 100 c.c. of blood in passing through the same range of reactions neutralise the equivalent of 100 c.c. of $N/100$-hydrochloric acid; the proteins are thus about one-fifth as efficient in maintaining the neutrality of normal blood. It cannot be inferred from this that the same holds for tissues and tissue fluids. The proteins of serum are precipitated by alcohol, not in the free form, but as salts. W. D. H.

The Morphological Detection of Methæmoglobin in the Blood. G. KRÖNIG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 539—546).—The change of the blood-pigment into methæmoglobin produced by certain poisons (chlorates, etc.) is well-known, and has been detected spectroscopically. The present paper deals with the microscopic changes the corpuscles undergo, and illustrations are given of their disintegration, the separation of pigment from stroma, the clumping of the hæmoglobin, its change into methæmoglobin with accompanying changes in staining reactions, and the ingestion of the red corpuscles in different stages of breakdown, or of the methæmoglobin granules by leucocytes. W. D. H.

The Capacity of the Animal Body to Produce Multivalent Precipitating Sera. CASIMIR STRZYZOWSKI (*Zeitsch. physiol. Chem.*, 1910, **66**, 1—7).—By immunising rabbits against several proteins the anti-serum obtained contains specific precipitins for each.

W. D. H.

Antitrypsin. S. COBLINER (*Biochem. Zeitsch.*, 1910, **25**, 493—504). —An investigation into the nature of the antitrypsin in serum, the

mechanism of its production, and the conditions influencing its variations in quantity. It has no lipoid character, but is a true antisubstance. In the human economy whenever excretion from the pancreas occurs, a part of the trypsin is always absorbed again. This acts as a hormone for the cells concerned, and a corresponding liberation of antitrypsin in the blood-stream takes place. G. S. W.

The Catalase Content of Maternal and Fœtal Blood and the Action of Fœtal Serum on Animals of the Same Species. GEORG LOCKEMANN and JOHANNES THIES (*Biochem. Zeitsch.*, 1910, **25**, 120—150).—The catalase content of rabbit's blood was estimated by measuring the amount of destruction of hydrogen peroxide solution (1%) which takes place when 30 c.c. are left for two hours with 10 c.c. of diluted blood (1 : 1000) at room temperature. It was found that the blood of the fœtus was poorer in catalase than the maternal blood.

The intravenous injection of small quantities of fœtal blood or serum into pregnant animals causes generally, in the case of rabbits, symptoms of illness, especially when the injection is repeated after several days. The symptoms vary in different cases, and in some cases are manifested in the form of tonic and clonic convulsions, which result finally in the death of the animal. In the case of non-pregnant animals, the first injection is without effect. A second injection after eight days, has an effect as powerful as that on pregnant animals. The results obtained are similar to those found in the phenomenon of anaphylaxis. For this reason, the author suggests that eclampsia may be allied to an anaphylactic action. S. B. S.

Poisonous Properties of Blood. J. STUDZINSKI (*Zentr. Physiol.*, 1910, **23**, Reprint 8 pp.).—The transfusion of blood from one animal to another of the same species usually provokes a temporary rise of blood pressure, whilst when the second animal is of a different species, a temporary fall of pressure occurs. In some cases, however, these phenomena are reversed. The lowering of pressure is ascribed to the presence of vasodilatin (compare Popielski, Abstr., 1909, ii, 593) in the injected blood. A second injection made after the effects of a previous one have passed off, has no marked action. A solution obtained by adding to defibrinated blood phosphotungstic acid, and removing the excess of this reagent with barium hydroxide, was just as active as the blood itself. This solution when evaporated to one-fourth of its volume and injected into a dog (15 c.c. per kilo. of body-weight) causes the death of the animal, and the heart is found in a condition of extreme diastole. The vasodilatin is soluble in absolute alcohol, and is not precipitated from that solvent by a moderate quantity of ether. The rise of pressure occurring in some cases is said to be due to *vasohypertensin*, solutions of which can be obtained by similar methods. R. V. S.

Analytical Investigations on Nitrogen and Phosphorus Metabolism and their Relationships. GEORG GRUND (*Zeitsch. Biol.*, 1910, **54**, 173—229).—The simple balance-sheet method of comparing ingesta and egesta cannot settle the question of the

intimate changes which occur in the organs. In the present research on dogs and hens, the organs themselves were investigated, after being freed from blood. In rich protein feeding, the liver takes up more protein, and in hunger loses more than do the kidneys and muscles. The relationship of total phosphorus to total nitrogen in the dog's organs remains fairly constant ($P_2O_5 : N = 1 : 7·1$); in the hen, the quotient is constant for the muscles, but in the liver it sinks slightly on protein feeding, and rises greatly on vegetable food rich in phosphorus. The quotient of protein phosphorus to protein nitrogen in the dog's liver on a protein diet sinks to a small degree, and is probably due to changes within the cells. The quotient of residual to total nitrogen shows great variations, and no general rules can be stated. The quotient of protein phosphorus to total phosphorus shows a slight fall in the dog's liver on protein feeding, and runs parallel to the quotient of protein phosphorus to protein nitrogen. W. D. H.

The Metabolic Influence of Copious Water Drinking with Meals. C. C. Fowler and Philip B. Hawk (*J. exper. Med.*, 1910, **12**, 388—410).—The subject of the experiment, a man aged twenty-two, took 3 litres of water daily with his meals for five days. His weight increased by two pounds, and there was an increase in urinary nitrogen, mainly in the form of urea, ammonia, and creatine; creatinine was diminished, probably because the water stimulates protein catabolism; creatine appeared probably because water causes a partial muscular disintegration; the ammonia increases probably because there is an increased output of gastric juice. The fæces, fæcal nitrogen, and fæcal bacteria all diminished. The protein constituents of the food were more economically utilised. The result indicates many desirable and no undesirable features. W. D. H.

The Influence of Fat Subcutaneously Administered on Protein Metabolism. Ernst Heilner (*Zeitsch. Biol.*, 1910, **54**, 54—63).—Metabolic experiments on rabbits are described, in which the administrations of olive oil by the mouth and subcutaneously are compared. The oil was given in amounts sufficient to satisfy the caloric need of the body; subcutaneous administration did not affect fat metabolism, but raises protein catabolism; the absorption of food so given is very slow, and subcutaneous feeding on fat cannot be recommended for clinical use. W. D. H.

Nuclein Metabolism in the Pig. Alfred Schittenhelm (*Zeitsch. physiol. Chem.*, 1910, **66**, 53—69).—Nucleic acid administered to pigs is acted on by nuclease, deamidase, and oxydases; purine bases and uric acid are formed, and a final product is allantoin, which accounts for a small fraction (1—5% only). The purine bases in pig's urine consist mainly of xanthine and hypoxanthine; a small amount of adenine is present, but no guanine. Pecile found guanine in the urine of a pig suffering from gout, and further investigation of the metabolism in gouty pigs is desirable. W. D. H.

Effects of Nutrition with Maize. Action of the Gastric Juice on Zein and Gliadin. II. Silvestro Baglioni (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 512—517).—The author's experiments on the

action of the gastric juice of the dog on zein and gliadin show that the juice has a twofold action on gliadin. In the first phase of the action, the gliadin is degraded into simpler protein products (peptones, gliadoses), the latter being subsequently converted into compounds which are deposited from the liquid as precipitates. The biuret reaction is red during the earlier stages of the reaction, but changes later to violet. As this second action can be prevented by previous heating of the liquid to 92°, it appears to be a true enzymic action. Zein offers considerably more resistance to the action of gastric juice than does gliadin, and it is converted into peptone-like products or zeoses, which are unchanged by further action of the juice. T. H. P.

The Nutritive Value of Fish in Comparison with Beef and its Effect on the Urine. B. SLOWTZOFF (*Zeitsch. physikal. diätet. Therapie*, 1910, **14**, 1—20).—Fresh or smoked fish has the same nutritive value as beef, but salted and dried fish is less readily absorbed. As compared with beef, less of the nitrogen leaves the body as urea, and more as residual nitrogen. Urinary indican is increased on a fish diet, but diminished if the fish is cured. Fresh (but not cured) fish increases the absorption of salts in the intestine, and acts favourably on phosphorus and magnesium metabolism; the retention of calcium is smaller on a fish diet. W. D. H.

Purine Metabolism. II. The Capacity for Destroying Uric Acid of the Organs of Scyllium catulus. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, **25**, 296—300).—The spleen and Wolff's bodies were inactive; kidneys, stomach, intestine, and muscular tissue possess the capacity for destroying uric acid; in the case of the liver, the reaction follows the type of a unimolecular reaction. The reaction is a fermentative process, at any rate in the case of the liver, which is rendered inactive by boiling. S. B. S.

Purine Metabolism. III. The Total Nitrogen and Purine Nitrogen in the Organs of Scyllium catulus. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, **25**, 411—414).—The author tabulates the results of analyses of the principal organs, those containing the largest amount of purine substances being the pancreas, testicle, and spleen. S. B. S.

Purine Metabolism. IV. The Behaviour of the Purine Substances in the Autolysis of the Liver of Scyllium catulus. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, **25**, 415—419).—A nuclease is present in the liver of *Scyllium catulus* which exerts its activity chiefly in the interval between the sixth and twenty-fourth hour of autolysis. The purine bases separated from nucleoproteins by this nuclease are so changed in the process as to lose their character of purine substances. Uric acid could not be detected as a product of the change. S. B. S.

The Decomposition of Cellulose in the Horse's Cæcum. HEINRICH VON HOESSLIN and E. J. LESSER (*Zeitsch. Biol.*, 1910, **54**, 47—53).—Scheunert's conclusion is confirmed, that the decomposition

which occurs in cellulose in the cæcum of the horse is due to the activity of micro-organisms. W. D. H.

Protein Degradation in the Intestine of Man. ALICE STAUBER (*Biochem. Zeitsch.*, 1910, **25**, 187—203).—The method was to observe the hourly output of urea after meals. A constant curve was found for normal individuals after a standard meal; in pathological cases, a deviation from the normal curve was detected. In normal individuals, after washing out the excess nitrogen by drinking large quantities of fluid before the test meal, it was found that the maximum of urea excretion took place between the fourth and fifth hour after the meal; the same fact was observed in several pathological cases. If degraded protein, such as peptones, be substituted for the standard protein of the normal meal, the maximum for the urea output is reached between the first and second hour after the meal. In tuberculous patients, this same maximum was noticed even after a normal meal not containing the degraded proteins. S. B. S.

The Real Relation of Trypsin to Erepsin. KARL GLAESSNER and ALICE STAUBER (*Biochem. Zeitsch.*, 1910, **25**, 204—218).—Both the small and large intestine contain in the mucous membrane an albumose-splitting enzyme, which is present in the larger quantity in the small intestine. This ereptic action is not due to coli bacilli. Trypsin and the pancreas also contain an ereptic component. The ereptic and tryptic ferment actions can be separated from one another by taking advantage of the fact that blood-serum inhibits only the tryptic action. If the pancreatic duct of a rabbit is ligatured, an increase of erepsin will be found both in the blood and in the small intestine. If the pancreas is destroyed by the injection of paraffin into the gut, erepsin disappears from the intestine. S. B. S.

The Influence of Sodium Glycocholate on Tryptic Digestion. G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1910, **25**, 220—238).—The rate of digestion was measured by means of the viscometer. No marked effect on the rate of tryptic digestion could be observed when small quantities of sodium glycocholate were added to the digestion mixture. S. B. S.

The Influence of Bile Salts on the Pancreatic Digestion of Starch. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1910, **25**, 239—256).—The viscometer method and estimation of maltose were the chief methods employed. It was found that the amount of sugar formed from starch as a consequence of the action of the pancreatic ferment did not depend on the time and amount of ferment present, being proportional neither to the one nor the other of these changeable factors. The curves therefore representing the rate of reaction are not straight lines, neither have they a simple logarithmic character, being similar in this respect to those representing the tryptic digestion of proteins. Bile salts exert a favourable influence on the rate of digestion, which is independent of the concentration of the ferment and of the time of digest. There is a certain optimum concentration for the favouring

action of bile salts, which is higher than that found normally under physiological conditions of digestion. S. B. S.

Physiology of Glands. XV. The Relationship between the Physico-chemical Properties of the Gland Proteins and the Secretive Capacity of the Glands. LEON ASHER and THEODOR KARAÚLOW (*Biochem. Zeitsch.*, 1910, **25**, 305—326).—The glands investigated were the pancreas and kidneys, from which the nucleoproteins were prepared. It was found that the internal friction of alkaline solutions of the nucleoprotein of kidneys was greater than that of those from the pancreas. Addition of electrolytes contained in blood-plasma diminished the viscosity of the solution of kidney nucleoprotein more than it did that of pancreas nucleoprotein. Dextrose showed no marked differential action. The conductivity of solutions of kidney nucleoprotein was greater than that of pancreas nucleoprotein. Addition of electrolytes increased the conductivity of a solution of nucleoproteins in $N/10$-potassium hydroxide more than it did the conductivity of protein-free $N/10$-potassium hydroxide. The effect was more marked in the case of pancreas nucleoprotein solution than in that of kidney nucleoprotein solution.

Measurement of *E.M.F.* in gas chains showed that pancreas nucleoprotein combines with more alkali than does kidney nucleoprotein. The authors explain the results by assuming that a combination of the nucleoprotein with electrolytes takes place, and explain the bearing of their results on Asher's theory, that the granules of the secreting cells act as condensers for substances that are afterwards secreted.

S. B. S.

The Relationship of Glycogen in the Frog's Ovary to the Time of Year. KAN KATO. **Glycogen in the Frog's Ovary.** MAX BLEIBTREU (*Pflüger's Archiv*, 1910, **132**, 545—579, 580—599).—The maximum of glycogen in the frog's body occurs in October and November; it sinks during the winter, and a further drop occurs at the spawning season, although even then the body contains a good deal. The liver glycogen follows the same order. The weight of the ovary rises from September to March; the great increase of weight which occurs in April is largely due to water; the glycogen of the ovary is least in the autumn and winter; it rises enormously in the spring, and reaches its maximum at the spawning time, so that more than half of the total glycogen of the body is then contained in the ovary and the eggs.

The second paper fills in some of the details in Kato's work, the results of which are generally confirmed in several species of frog.

W. D. H.

Oxidations in Living Cells (Sea Urchin). OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1910, **66**, 305—340).—The main estimations made were of oxygen; after fertilisation, the amount used by the egg greatly increases; the addition of phenylurethane to the sea water depresses cell division, but leaves the oxygen consumption almost unchanged. The action of various agents and reagents on

the oxygen consumption was investigated, such as hydrogen ions, hydroxyl ions, various salts and metals, etc. The results are discussed in relation to Loeb's theory of fertilisation and membrane formation, and Overton's theory of narcosis. The importance of intracellular enzymes was not confirmed. W. D. H.

Autolysis of Fertilised and Unfertilised Echinoderm Eggs. ELIAS P. LYON and L. F. SHACKELL (*J. Biol. Chem.*, 1910, **7**, 371—378).—*Arbacia* eggs autolysed in chloroform water show an increase of soluble nitrogen in periods varying from days to months; this occurs in acid solutions only. Fertilisation exerts little or no effect. More than one-sixth of the soluble nitrogen is of protein origin; the autolysis of phosphorus is parallel to that of nitrogen. With sperm a similar autolysis occurs, except in acid solutions. W. D. H.

The Enzymes which Act on Disaccharides in the Human Embryo and New-born Child. I. JUSSUF IBRAHIM (*Zeitsch. physiol. Chem.*, 1910, **66**, 19—36).—In new-born children, lactase, maltase, and invertase are present in the mucous membrane and contents of the small intestine. In the contents of the large intestine, little or no lactase is found. Invertase appears about the beginning of the fourth month of fœtal life, maltase at the end of the same month, and lactase about the eighth month. In the new-born child, invertase and lactase occur in the intestine only; maltase is also present in the blood and pancreas. W. D. H.

The Enzymes which Act on Disaccharides in the Human Embryo and New-born Child. II. JUSSUF IBRAHIM and L. KAUMHEIMER (*Zeitsch. physiol. Chem.*, 1910, **66**, 37—52).—Observations by Plimmer's method show that lactase is the last formed of the enzymes which act on disaccharides, and probably is the last digestive enzyme formed in fœtal life. W. D. H.

The Analysis of Brain, Especially with Regard to the Content in Cholesterol and Fatty Acids. NIRO MASUDA (*Biochem. Zeitsch.*, 1910, **25**, 161—164).—The cholesterol was estimated by Kamagawa and Suto's method, and in addition, the water, solid matter, total nitrogen and phosphorus, higher fatty acids, total ash, and ash insoluble in water were estimated in the cerebrum, midbrain, and cerebellum from brains of man, ox, horse, and pig. The author tabulates his results. S. B. S.

The Constituents of the Tissues which are Concerned in the Wassermann Reaction, Especially Lecithin and Cholesterol. CARL H. BROWNING, J. CRUICKSHANK, and I. MCKENZIE (*Biochem. Zeitsch.*, 1910, **25**, 85—87 *).—Fresh ox-liver was extracted with ethyl acetate at 60°. The part that separated on cooling was dissolved in ether and precipitated with acetone, which treatment was repeated twice. The properties of the part soluble in ethyl acetate and those of the other fraction ("pure lecithin") were investigated

* and *J. Path. Bact.*, 1910, **14**, 484—502.

with reference to the following reactions: (*a*) hæmolytic action, (*b*) capacity for activating cobra hæmolysis, (*c*) inhibitory action on the serum complement, and (*d*) the capacity to act as antigen in the Wassermann reaction. Amongst other results, it was found that alcoholic lecithin solution is capable of dissolving relatively large amounts of cholesterol, and that such a solution is a very efficient substitute for the ordinary tissue extract in Wassermann's reaction.

S. B. S.

Investigations on Smooth Muscle (Dog's Oesophagus). II. Action of Cations. G. FIENGA. **III. Replacement of Calcium in So-called Physiological Fluids.** GIUSEPPE BUGLIA (*Zeitsch. Biol.*, 1910, **54**, 230—248, 249—268).—II. The cations investigated fall into two groups: (1) those which increase muscular tonus—potassium, calcium, strontium, barium, and mercury; (2) those which have the opposite effect—lithium, ammonium, sodium, magnesium, manganese, cobalt, nickel, zinc, and cadmium. There is a difference of intensity in the actions of the various metals, in the reversibility of the action, and in the antagonism of members of the two groups.

III. The replacement of the potassium in Ringer's fluid by various other metals was investigated, but the only one found to give equally good results was cæsium.

W. D. H.

The Presence of Iron-containing Lipoids in the Spleen. ROBERT BUROW (*Biochem. Zeitsch.*, 1910, **25**, 165—170).—The chief lipoid isolated from human spleen was a saturated compound containing 1·37% phosphorus, 0·41% iron, and 1·23% nitrogen (N : P = 2 : 1). In addition, two other iron-containing unsaturated phosphatides were obtained, together with jecorin, lecithin, and cholesterol. The author does not give the methods of preparation.

S. B. S.

Adrenalectomy and Glycosuria. HUGH MCGUIGAN (*Amer. J. Physiol.*, 1910, **26**, 287—294).—Removal of the adrenals in rabbits renders the production of salt glycosuria impossible, while phloridzin glycosuria occurs readily. Removal of the adrenals in dogs makes the production of salt glycosuria difficult, but not impossible, and in cats the same operation does not modify the production of salt glycosuria.

W. D. H.

The Cholesterol Ester of the Horny Layer. P. G. UNNA and L. GOLODETZ (*Biochem. Zeitsch.*, 1910, **25**, 425—426).—The authors aver that Salkowski's discovery of esters of palmitic acid in specimens from cases of dermatitis exfoliativa is not definitely substantiated, chiefly on the ground that a lanolin ointment might have been employed in the treatment of these cases, and that the palmitic esters were derived from this source.

S. B. S.

The Cholesterol Esters of the Horny Layer. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1910, **25**, 427—428).—A reply to Unna and Golodetz (preceding abstract). The author denies the possibility

of the palmitic ester having been derived from lanolin on the ground that the latter on extraction with 93% alcohol never yields snow-white needles melting at 77—78°. S. B. S.

The Importance of Iron for Animal Oxidations. ERNST MASING (*Zeitsch. physiol. Chem.*, 1910, **66**, 262—264).—Whether cells and cell nuclei or their nucleoproteins contain iron has been answered differently by former workers. In the present research, cells were selected rich in nuclear material, and from organs (generative organs) where oxidation is vigorous; care was also taken to avoid contamination with hæmoglobin. The sperm of the sea urchin and salmon, and the eggs of the sea urchin, contain the merest traces of iron, in many cases not more than there is in sea-water; it is regarded as doubtful whether iron is really important for oxidative processes. W. D. H.

The Influence of Certain Toxins and Antitoxins on the Oxidising and Reducing Capacities of the Tissues. I. ANDREA PITINI (*Biochem. Zeitsch.*, 1910, **25**, 257—261).—The action of diphtheria- and typhus-toxins on the oxidation and reduction processes in rabbits was investigated. The oxidation processes were investigated by Nencki's method, namely, by determining the amount of phenol excreted after the injection of benzene in the animals. The reduction processes were investigated in both the alcoholic and aqueous extracts of the muscular tissue by the method of Helier and Richet. Both typhus- and diphtheria-toxins were found to increase the reduction capacity, and diminish the oxidising capacity of the tissues.

S. B. S.

Glycolytic Process with Reference to the Work of Stoklasa, Oppenheimer, and Rosenberg. J. DE MEYER (*Zentr. Physiol.*, 1910, **23**, 965—974).—Mainly polemical. The views advanced may be summarised as follows: The glycolytic power of the tissues is not proved to be due to an enzyme secreted by the tissue cells, but is probably the result of the action of an enzyme in the blood on these tissues. he pancreas does not form a glycolytic enzyme, but the favourable action of pancreatic extracts on the glycolysis produced by blood is due to the presence of an amboceptor or activator in the pancreatic extracts. W. D. H.

The Amount of Choline in Animal Tissues. TOSAKU KINOSHITA (*Pflüger's Archiv*, 1910, **132**, 607—631).—The delicacy of the various tests which have been proposed for choline are compared. For quantitative purposes, Lohmann's method of preparing it from the tissues was employed; it is then weighed as the gold compound, various precautions to prevent loss being described. The intestine, pancreas, spleen, muscle, liver, kidney, and lung all contain choline in amounts varying from 0·01 to 0·03%. W. D. H.

Adenase and its Relationship to the Origin of Hypoxanthine in the Organism. CARL VÖGTLIN and WALTER JONES (*Zeitsch. physiol. Chem.*, 1910, **66**, 250—256).—It is pointed out that the

existence of hypoxanthine in a tissue is not a necessary proof of the existence of adenase, an enzyme which converts adenine into hypoxanthine. There are cases, for instance, dog's muscle, where adenase is absent and hypoxanthine present. The importance of the purine enzymes seems to have been exaggerated ; at any rate, the following facts point to the existence of other factors as well: 1. The organs of the rat show no purine enzymes ; nevertheless rat's urine contains uric acid. 2. The organs of the ape contain such enzymes, but the urine contains little or no uric acid. 3. Ascoli's work on the physiological synthesis of uric acid shows that this may occur when neither a purine ring nor a purine enzyme is present. W. D. H.

A New Mode of Formation of β-Hydroxybutyric Acid in the Animal Organism. HENRY D. DAKIN (*Journ. Amer. Medical Association*, 1910, **54**, 1441).—The author finds that acetoacetic acid is reduced to β-hydroxybutyric acid in the animal organism. In experiments in which a quantity of about 10 grams of acetoacetic acid in the form of its sodium salt (8% solution) was injected intravenously into cats and small dogs in the course of four to six hours, the urine secreted during this period was found to contain more than 1 gram of *l*-β-hydroxybutyric acid.

β-Hydroxybutyric acid and acetoacetic acid are thus mutually interconvertible in the animal organism according to whether oxidation or reduction takes place. Since β-hydroxybutyric acid when present in the urine of diabetics is almost invariably accompanied by acetoacetic acid, it is possible that some part of the former acid may be derived by the reduction of acetoacetic acid. W. D. H.

Origin of the Brown Pigment in the Integument of the Larva of Tenebrio molitor. ROSS A. GORTNER (*J. Biol. Chem.*, 1910, **7**, 365—370).—The process of coloration in the larva is due to the interaction of an oxydase and a chromogen; it proceeds in the absence of life. It can be inhibited by carbon dioxide and by nitrogen, but proceeds again when oxygen is admitted and the inhibitor removed. The chromogen resembles tyrosine in being not precipitable by phosphotungstic acid. In the pupa stage, the chromogen is absent, but tyrosinase is present both in the pupa and the beetle. A phenolic substance is present in the larva, as also are substances capable of uniting with diazo-compounds to form azo-dyes.
W. D. H.

Chemistry of Acute Falls in Weight. Relationships between Water and Salts in the Organism. LUDWIG TOBLER (*Arch. exp. Path. Pharm.*, 1910, **62**, 431—463).—Acute loss of body-weight was produced in dogs by the administration of large doses of magnesium sulphate, and death ensues in a few days when the body has lost from 25 to 30% of its weight. The skin and muscles lose most weight, 65% of the total, and half of this is due to loss of water. These parts, however, contain after death 65 to 75% of water, the normal figure being 55%. The different mineral constituents are lost in varying proportions, the greatest loss next to water falling on the chlorine and potassium. Similar conditions obtain after great loss of water by the skin. W. D. H.

Biological Differentiation of Milk and Milk Proteins. FRITZ KOLLMEYER (*Zeitsch. Biol.*, 1910, **54**, 64—90).—The capacity to unite with complement renders it possible to differentiate milks biologically; the action is specific, and each protein (caseinogen and the albumin-globulin complex) has its own special action. Milk can by this means be distinguished from serum. In addition to the specific milk proteins, proteins are present in the milk identical with those in the blood, and such proteins are more abundant in colostrum than in fully formed milk. Milk which has been boiled can also be used for the preparation of an anti-serum which reacts with boiled and raw milk. The union with complement of milk antisera, and the action of the antigens does not appear to be dependent on the calcium present. W. D. H.

Comparative Investigation on the Composition of Caseinogen from Human and Cow's Milk. EMIL ABDERHALDEN and LEO LANGSTEIN (*Zeitsch. physiol. Chem.*, 1910, **66**, 8—12).—So far as total hydrolysis is concerned, the yield of individual amino-acids indicates no difference in the composition of the caseinogen of cow's and human milk. W. D. H.

Comparison between the Mode of Action of Certain Retarding Salts and the Proteins of Milk Coagulable by Heat on the Coagulation by Rennets of Boiled Milk. C. GERBER (*Compt. rend.*, 1910, **150**, 1357—1360. Compare this vol., ii, 527).—An account of further experiments in support of the theory previously advanced, that those substances which protect fresh milk from coagulation by ferments which act on boiled milk do so by combining with the casein, and are not strictly speaking anti-ferments. Boiled milk containing small quantities of salts of copper, silver, mercury, gold, or metals of the platinum group behaves towards ferments precisely as fresh milk in the absence of these substances. The protective influence of these salts closely resembles that exerted by those proteins of fresh milk which are rendered insoluble by the action of heat. W. O. W.

Ferments of Milk and their Origin. JULIUS WOHLGEMUTH and MICHAEL STRICH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 520—524). —It is known that the milk of most animals contains carbohydrate- and fat-splitting ferments, and also an oxydase, reductase, and catalase. A proteoclastic enzyme has so far not been found. The *casease* of Duclaux, which possesses the property of dissolving the casein coagulum formed by rennet, is not normally present in fresh milk, but is the product of the growth of a definite organism. The galactase of Babcock and Russell (compare Abstr., 1900, i, 712) has similar origin. The statement of Spolverini that milk contains pepsin and trypsin, and the researches of Moro are similarly discredited. The authors succeeded in demonstrating the presence of a glycyl-tryptophan-splitting ferment in human milk, and in the milk of the rabbit, cow, goat, and guinea-pig. It was found most abundantly in the first two instances. The ferment is killed in fifteen minutes at 65—70°, but withstands peptic digestion. The rôle of this enzyme in the economy of infantile

nutrition is at present open to question. The possibility of accurate quantitative estimation of diastase in these liquids led the authors to endeavour to discover the origin of these milk ferments by the examination of the diastatic content of the blood, urine, and milk of various animals. Guinea-pigs have more diastase in their blood than dogs, dogs more than rabbits. The diastatic content of the milks of these animals is, however, in the reverse order. From one woman, milk, blood, and urine were obtained. The diastatic contents of these liquids were of the order 200 : 1 : 1 during the earlier period of lactation, and at a later period a comparison of milk and blood gave the value of diastatic activity 10 : 1. Colostrum contains even more diastase than milk during earlier lactation. Cow's and goat's milk contains no diastase, although the blood of these animals has the same diastatic content as that of woman. The conclusion is drawn that the mammary glands of some animals have special capacity for secretion and excretion of blood-diastase, although most of the milk diastase, where it occurs, is elaborated in these glands. It is suggested that these glands are the seat of formation of the other enzymes present in milk. That blood diastase can pass into milk was shown by direct experiment. In three instances it was demonstrated that ligaturing the pancreatic duct of a bitch in early lactation produced a great increase of diastase in the blood, urine, and milk. The increase in the blood was much greater than that in milk. The diastatic content of the milk and of the blood returned to normal simultaneously. G. S. W.

Accidental Presence of Thiocyanates in Milk and their Origin. E. D. STŒCKLIN and CROCHETELLE (*Compt. rend.*, 1910, **150**, 1530—1531).—Samples of milk showing a rose-red coloration were found to contain thiocyanates. The presence of these substances was traced to the occurrence of mustard oil (from *Cruciferae*) in cattle-cakes on which the cows had been fed. W. O. W.

The Fate of the Intermediate Uric Acid in Human Metabolism, and the Allantoin Content of Human Urine; the Recognition and Stability of Allantoin. WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1910, **25**, 431—459. Compare Abstr., 1907, ii, 284).—In dogs, nucleic acid given by the mouth is converted, almost quantitatively, into allantoin. Rabbits yield only 40—50% of the nitrogen of nucleic acid in this form. Normal human urine may contain from 5—50% of the ingested purine nitrogen as uric acid. Given subcutaneously, uric acid appears as allantoin for the most part in the case of the dog and rabbit, whilst in the human being about 90% is excreted unaltered, a small fraction not being recovered. The author, disagreeing with Schittenhelm and others, asserts that allantoin, as in other mammals, is produced in the purine metabolism of the human being, but in so small an amount that uric acid must be regarded as the main channel of excretion of purine nitrogen. In the method employed, the urine is put through a lengthy series of precipitation processes in which phosphotungstic acid and mercury, lead, and silver salts are employed. Finally, the free allantoin is recrystallised from hot water and weighed. A critical examination of the method and its suggested modifications is given.

Pure allantoin undergoes slight decomposition when boiled in solution in distilled water. In a similar manner to uric acid, it yields oxalic acid on shaking with alkali hydroxides. It reduces solutions of certain metallic salts, yields glyoxalic acid on oxidation, and may be used instead of that acid in the Adamkiewicz's reaction. G. S. W.

Chylous and Pseudo-chylous Ascites. R. L. MACKENZIE WALLIS and H. A. SCHÖLBERG (*Quar. J. Med.*, 1910, **3**, 301—312).—The milky appearance of a pseudo-chylous ascitic fluid is due to a lecithin-globulin complex which is held in suspension by the inorganic salts present; removal of the latter by dialysis precipitates the complex, and the opalescence disappears. The milky appearance is not due to free fat, lipoids, or mucinoid material. W. D. H.

The Etiology of Beri-Beri. S. KAJIURA and OTTO ROSENHEIM (*J. Hygiene*, 1910, **10**, 49—55).—Beneficial results have been achieved in Japan by merely replacing a certain percentage of rice by other nitrogenous foodstuffs (meat or barley); this is strongly in favour of the view that the disease beri-beri is not produced by a specific poison in rice, but by the unphysiological nature of a rice diet. Rice is poor in calcium and phosphorus; its nitrogen percentage is not markedly lower than that of barley. The beneficial results of barley might therefore be due to the nature of its proteins. The gliadins or alcohol soluble proteins in barley are represented by hordein, and they are absent in rice, and, possibly, this absence will explain the non-efficiency of a rice diet. On this hypothesis, experiments on fowls were undertaken with white or peeled rice from Japan. A simple diet of this rice causes in these birds a fatal disease identical with, or very similar to, beri-beri, independently of influences of climate or locality; the addition of hordein in the quantities used, or of large quantities of calcium carbonate or phosphate, did not, however, prevent the disease. W. D. H.

Biochemistry of Growth. I. The Total Nitrogen Metabolism of Rats Bearing Malignant New Growths. II. Distribution of Nitrogenous Substances in Tumour and Somatic Tissues. WILHELM CRAMER and HAROLD PRINGLE (*Proc. Roy. Soc.*, 1910, *B*, **82**, 307—315, 315—320).—Less nitrogen is necessary to build up tumour tissue than the same weight of somatic tissue. Animals with tumours maintain a positive nitrogen balance, and the nitrogen retention increases with the size of the tumour. The tumour cells have no special affinity for nutritive material, nor do they proliferate at the expense of the other tissues; their nitrogenous material is derived from a sparing action on protein metabolism. No evidence of a toxin was found. Weight for weight cancer cells contain only about three-quarters of the protein in ordinary tissue cells, so that a large mass of tumour is built from a comparatively small weight of protein food; the abiuretic products, however, are slightly more abundant in cancer than in normal cells. Fœtal tissues and probably other rapidly growing tissues have also a relatively low nitrogen percentage. W. D. H.

Peptolytic Enzymes in Cancer and other Tumours. III. EMIL ABDERHALDEN and FLORENTIN MEDIGRECEANU. **IV.** E. ABDERHALDEN and LUDWIG PINCUSSOHN (*Zeitsch. physiol. Chem.*, 1910, **66**, 265—276, 277—283).—III. The various tumours of rats and mice investigated always contain peptolytic enzymes, but with one exception no difference between these and those of normal liver cells were noted. In some cases, the tissue juice of ulcerated tumours acted more vigorously than that of non-ulcerated tumours. The exception just alluded to is that the juice of all the mouse tumours and most of those from rats produces cleavage of silk-peptone, whereas that of normal tissue does not. The serum of normal rats cleaves glycyl-*l*-tyrosine and *dl*-leucyl-glycine; that of mice cleaves the first-named dipeptide; the second was not investigated. It is probable that the serum of dogs (which normally contains no peptolytic enzymes) with tumours contains such enzymes.

IV. The difference just noted in animal tumours holds also for those in man, and may be of diagnostic value. W. D. H.

Effect of Electric Bath Treatment of the Insane on the Urinary Creatinine. R. L. MACKENZIE WALLIS and EDWIN GOODALL (*J. Mental Sci.*, April, 1910).—The excretion of creatinine in the insane is usually low; it is not influenced by ordinary warm baths, but electric baths using the sinusoidal current slightly increase it, possibly by the effect on the muscles. W. D. H.

Choline in Pathological Cerebro-spinal Fluid. MAX KAUFFMANN (*Zeitsch. physiol. Chem.*, 1910, **66**, 343—344).—The present tests for choline are not regarded as satisfactory, but the base which has been described as such in normal and pathological cerebro-spinal fluid is "certainly not choline." What it is is left uncertain, as the author had the misfortune to lose the greater part of the substance he had collected from six and a-half litres of fluid.

W. D. H.

The Non-coagulable Nitrogen of Sera of Normal, Syphylitic, and Tumour Cases. M. TAKEMURA (*Biochem. Zeitsch.*, 1910, **25**, 505—507).—An investigation of the "non-coagulable nitrogen" of certain normal and pathological sera before and after autolysis at 55°. The "total nitrogen" of serum from patients with tumours is not greater than in normal cases. Before autolysis, there is more coagulable nitrogen than the normal in carcinoma cases. After autolysis, the sera of carcinoma cases again gave higher "non-coagulable nitrogen" values than the normal and sarcoma cases; in three syphylitic cases having a positive Wassermann reaction, the sera had normal values; in three cases of paralysis were found still more non-coagulable nitrogen than in the cancerous patients.

G. S. W.

Phosphorus-content of Sera in Normal, Syphylitic, and Carcinoma Cases. M. TAKEMURA (*Biochem. Zeitsch.*, 1910, **25**, 508—509).—Small differences were observed between the values for the total phosphorus-content of the sera examined. Those giving a

positive Wassermann's reaction for syphylis contained more phosphorus than normal. The sera of carcinoma patients gave similar results.

G. S. W.

Behaviour of Elementary Sulphur in the Animal Organism. ARTUR KONSCHEGG (*Arch. exp. Path. Pharm.*, 1910, **62**, 502—517).—Administration of sulphur to dogs produces a rise in the total sulphates and the "neutral sulphur" of the urine, as previous observers have stated. There is also a marked increase in the ethereal sulphates, due almost exclusively to increase in the phenolsulphuric acid; the indoxyl sulphate hardly alters at all. The urinary nitrogen is unaltered. The drug almost always produces diarrhœa, and the sulphates of the fæces are increased. W. D. H.

The Formation of Ethereal Sulphates from Thiocarbamide. NIRO MASUDA (*Zeitsch. physiol. Chem.*, 1910, **67**, 28—34).—Thiocarbamide given subcutaneously in rabbits increases the "neutral sulphur" of the urine markedly; it is also in part found as such, and part as ethereal sulphate. Increase in the latter is therefore not primarily due to administration of phenol, as some have supposed.

W. D. H.

The Composition of Blood, Urinary Excretion, and Lymph Formation after the Intravenous Injection of Solutions of Colloids alone and in Conjunction with Crystalloids. ANGELO PUGLIESE (*Zeitsch. Biol.*, 1910, **54**, 100—152).—The diuretic action of hypertonic solutions of sodium chloride shows very small changes whether the salt is injected into the blood alone or in combination with gelatin and gum arabic, but the excretion of the salt occupies a longer time. The solids of the blood undergo a diminution if the salt solution is hypertonic or hypotonic and mixed with the colloid; in the former case, the osmotic pressure is raised, and in the latter it falls: this outlasts the diuretic effect. If the salt alone is injected, the blood is at first diluted, but soon it becomes more concentrated. The crystalloid and colloid mixture also causes a great increase in the lymph flow, and the osmotic pressure and chloride concentration of the lymph are raised. W. D. H.

Decomposition of Chloroform in the Organism. MAURICE NICLOUX (*Compt. rend.*, 1910, **150**, 1260—1263).—From experiments on dogs, in which the animals were placed in a globe and treated with air containing a known proportion of chloroform vapour, the total amount of chloroform eliminated also being determined, the author arrives at the conclusion that during anæsthesia and the period of recovery about 50% of the chloroform fixed by the blood and tissues undergoes decomposition. Experiments in which anæsthesia was effected by ingestion of chloroform water led to the same result.

W. O. W.

The Behaviour of Furylpropionic Acid in the Animal Body. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1910, **25**, 272—283).—After

administration of furylpropionic acid to a dog, furylacryluric acid was the main product recovered in the urine, the quantity obtained being equivalent to 21·5% of the furylpropionic acid administered. About 18·5% was recovered as pyromycuric acid, so that about 40% of the furylpropionic acid administered escaped destruction. The author gives synthetical methods for preparing the various substances in question. Pyromycuric acid (m. p. 165°) was obtained by the action of pyromucyl chloride on glycine. Furylacryluric acid (m. p. 218—219°) was obtained by the action of furylacryl chloride (m. p. 34°) on glycine, and furylpropionyluric acid (m. p. 118°) by the reduction by sodium amalgam of furylacryluric acid. S. B. S.

Pharmacological Action of Harmaline. JAMES A. GUNN (*Trans. Roy. Soc. Edin.*, 1910, **47**, II, 245—272).—Harmaline resembles quinine in being relatively much more toxic to mammals than to frogs. In the cases of the guinea-pig, rabbit, and cat, doses exceeding about 0·1 gram per kilogram were fatal, whilst for frogs the minimum lethal dose is 0·25 gram per kilogram. The pharmacological action of the substance also resembles quinine, in that it is of a non-selective type; it affects specialised tissues, such as voluntary muscle and the muscle of the heart, blood vessels, and uterus, and the cells of the central nervous system, whilst its action on less highly differentiated cells (protozoa, ciliated epithelium) has already been observed. In frogs, lethal doses rapidly produce paralysis of respiration, and in mammals, arrest of respiration due to paralysis of the respiratory centre is the chief cause of death from harmaline poisoning.
R. V. S.

The Behaviour of Mono-palmityl-*l*-tyrosine, Distearyl-*l*-tyrosine, and *p*-Aminotyrosine in the Organism of an Alcaptonuric Person. EMIL ABDERHALDEN and RUDOLF MASSINI (*Zeitsch. physiol. Chem.*, 1910, **66**, 140—144).—The question whether the compounds of fatty acids and aromatic amino-acids can be broken up by the body cells was investigated by giving them to an alcaptonuric patient; in spite of a deleterious effect which they exert on metabolism, the question is answered in the affirmative, for the homogentisic acid which originates from tyrosine was increased in the urine.

A similar result as judged by an increase in the reducing power of the urine followed the administration of *p*-aminotyrosine.
W. D. H.

Pharmacological Properties of Picric Acid. FRANCESCO MOTOLESE (*Arch. Farm. sperim. Sci.*, 1910, **9**, Reprint, 47 pp.).—With both leucocytes and infusoria, picric acid in the concentration 1 : 2000 coagulates the protein matter, and thus exerts an immediate fixing action. At the concentration 1 : 10,000, the acid does not injure the vitality of the infusoria, on which it exerts a marked negative chemotactic action; with the leucocytes, the vital manifestations are depressed and death ultimately caused, owing to the solution of the protoplasm, the same action being produced, although more slowly, at

the concentration 1 : 20,000. In the proportion 1 in 30,000, the acid is inactive towards the leucocytes. Picric acid has an astringent action superior to that of zinc sulphate, alum, or lead acetate, and almost equal to that of basic lead acetate. The acid is possessed of considerable diffusivity, owing to the fact that it is an electrolyte. The permeability of the cornea to picric acid is very slight, and less than that of the conjunctiva. T. H. P.

Pharmacological Action of Protocatechyltropeine. CHARLES R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1910, **47**, II, 273—285. Compare Jowett and Hann, Trans., 1906, **89**, 364).—From experiments on anæsthetised rabbits and cats, and on frogs, the author finds that protocatechyltropeine when subcutaneously administered paralyses the vagal endings in the heart, but is much less powerful than atropine or even homatropine. In certain doses, it paralyses the respiration temporarily; this action is due to paralysis of the respiratory centre, and not to a peripheral action. A gradual fall of blood pressure usually occurs, but this does not seem to be connected with the action on the respiration. In cats, a rise of blood pressure is sometimes observed, owing to the paralysis of the vagal endings. It was not found possible to show any separate pharmacological actions of the two groupings in the compounds. R. V. S.

The Behaviour of Phloridzin after Extirpation of the Kidneys. KARL GLAESSNER and ERNST P. PICK (*Pflüger's Archiv* 1910, **133**, 82—86).—Polemical against Leschke (this vol., ii, 530). The authors considers that his work, so far from contradicting, confirms their own. W. D. H.

Strophanthus sarmentosus; its Pharmacological Action and its Use as an Arrow Poison. SIR THOMAS R. FRASER and ALISTER T. MACKENZIE (*Trans. Roy. Soc. Edin.*, 1910, **47**, II, 341—410).—The alcoholic extract of the mature seeds of this plant contain a substance having the properties of a glucoside. On adding concentrated sulphuric acid to the dry extract, a brown colour, becoming violet, is developed. The pharmacological action of the extract is very similar to that of *S. hispidus* (compare Abstr., 1890, 262), the chief features of its action being the effects on the heart and skeletal muscles. Certain arrow poisons used in Nigeria, and said to be prepared from this plant, were found to behave physiologically in the same way as the alcoholic extract, so that in all probability they are obtained from that source. R. V. S.

Pharmacological Action of Tutu, the Toot Plant of New Zealand. CHARLES R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1910, **47**, II, 287—316).—The author has arrived at conclusions in agreement with those of Fitchett and Malcolm (Abstr., 1909, ii, 919) in respect of the experiments common to both investigations. The epileptiform convulsions caused by tutin are mainly of cortical and pontine origin, and the convulsions arising in the pons are very susceptible to anæsthetics. In rabbits, all doses which produce an

obvious action cause a fall of body temperature. When heated on the water-bath for three hours with a 1% solution of hydrochloric acid, or when raised to boiling temperature with 1% sodium hydroxide or 0·05% calcium hydroxide, tutin is decomposed, and the decomposition products have no physiological action. Coriamyrtin, which is obtained from another species of *Coriara* (*C. myrtifolia*), is a more powerful convulsant than tutin, and it is more rapid and transient in its action. R. V. S.

Influence of Dietary Conditions on Physiological Resistance. NELLIS B. FOSTER (*J. Biol. Chem*, 1910, **7**, 379—419).—Some dogs were fed liberally, others scantily, on protein in order to test their relative resistance towards abrin and ricin poisoning. The total number of experiments is too small to exclude other factors, such as breed, idiosyncrasy, etc., for whether they succumbed or survived was not related at all to their diet. W. D. H.

The Toxicity of Atoxyl. K. MUTO (*Arch. exp. Path. Pharm.*, 1910, **62**, 494—501).—The lethal dose for a mouse weighing 10 grams is 0·003—0·005 gram; for a frog weighing 15 grams, about 0·005, and for rabbits about 0·2—0·3 gram per kilo. of body-weight. In dogs the most marked post-mortem signs are congestion and hæmorrhages in kidney, intestine, and heart. Estimations of the amount of the drug which passes into the urine in rabbits are given. W. D. H.

Biochemical and Therapeutical Studies on Trypanosomiasis. ANTON BREINL and MAXIMILIAN NIERENSTEIN (*Ann. Trop. Med. and Parasit*, 1909, **3**, 395—420).—The following conclusions were drawn as to the action of atoxyl: (*a*) after injection, a comparatively small amount combines through the amino-group with serum proteins and forms "atoxyl-serum"; the greater part is secreted in the urine partly unchanged as *p*-aminophenylarsinic acid, partly oxidised in the form of *p*-hydroxyphenylarsinic acid and as hydroxycarbaminophenylarsinic acid, and partly as free inorganic arsenic; (*b*) from atoxyl-serum, arsenic is set free through an oxidation process caused by the oxidative ferments present, and probably also by trypanosomes, whereby the aromatic nucleus is destroyed; (*c*) at the same time reduction takes place in the intestines, whereby atoxyl is reduced to aniline and arsenious acid; (*d*) the arsenic which is formed by oxidation acts in the nascent state on the trypanosomes.

The authors have investigated the trypanocidal action of a large number of other arsenic compounds and dyes on various animals, but without finding any with distinctly marked action. The substances investigated include acetylated atoxyl, salicylyl-atoxyl, formyl-atoxyl, sodium-*p*-hydroxyphenylarsinate, disodium azobenzene-4-arsinate, tetrasodium phenazine-4-arsinate, sodium di-*p*-aminophenylarsinate, sodium 4-acetylamino-3-methylphenylarsinate, and various derivatives of the same, and certain antimony compounds.

The authors give a résumé of various investigations on the resistance to atoxyl acquired by trypanosomes, and conclude that the immunity is often acquired against the "atoxyl-serum," and the resistance only holds good in the animal in which it is acquired.

They also give results of experiments on the time required for destruction of the trypanosomes in the bodies of various animals, and on the value of sub-inoculations. S. B. S.

The Physiological Action of Cyanamide and Some of its Derivatives. ALBERT STUTZER and JULIUS SÖLL (*Biochem. Zeitsch.*, 1910, **25**, 215—219).—The toxic dose of cyanamide for guinea-pigs was 0·4 gram per kilo. of weight. Dicyanamide given *per os* to a dog in doses of 5 grams per kilo. of weight, administered over five days, produced no toxic effect; toxic effects were observed, however, on guinea-pigs with smaller doses. The hydrochloride of guanylcarbamide was also non-toxic to dogs in relatively large doses, but produced toxic effects on guinea-pigs in smaller doses. Diguanidine hydrochloride, guanylcarbamidesulphonic acid, and guanidylacetic acid were found to be non-toxic. S. B. S.

Toxolecithides. JULIUS MORGENROTH and R. KAYA (*Biochem. Zeitsch.*, 1910, **25**, 88—119).—The experiments tend to show that the hæmolytic action of cobra-poison is of two-fold nature, and can be activated either by a serum complement like an ordinary amboceptor or by means of lecithin. The following facts support this hypothesis: hæmolysis in presence of serum takes place only at higher temperatures, whereas that in presence of lecithin takes place at 0°; if the cobra poison is heated to 80°, it almost loses its capacity of being rendered hæmolytic by the addition of the serum complement, whereas the property of being rendered hæmolytic by lecithin remains, although weakened; on treatment with acids or alkalis, the amboceptor-like property is destroyed, whereas the power of being rendered hæmolytic by lecithin remains intact after treatment with acids, and is destroyed to a small degree after treatment with alkalis. On allowing the cobra poison to remain with complement before adding the blood-corpuscles, the former is destroyed and no hæmolysis takes place. The complement-destroying property of the poison can be inhibited by a specific anti-toxin, such as Calmette's serum, which also inhibits the amboceptor-like function as regards hæmolysis. The amboceptor-like action of the poison is not typical, in that the supposed amboceptor cannot be bound by the blood-corpuscles, even in the presence of the complement; neither could any binding of the lecithide with blood-corpuscles be demonstrated. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Does Water Sterilised by Ultra-violet Light contain Hydrogen Peroxide? Sterilising Power of Hydrogen Peroxide. JULES COURMONT, TH. NOGIER, and A. ROCHAIX (*Compt. rend.*, 1910, **150**, 1453—1454. Compare Abstr., 1909, ii, 753).—The length

of time required to produce appreciable amounts of hydrogen peroxide when a quartz-mercury lamp is immersed in water renders it unlikely that the sterilising action of ultra-violet light is due to the formation of this substance. The authors were unable to detect hydrogen peroxide in water which had been in contact with the lamp for twenty minutes. Water containing *Bacillus coli*, which was sterilisable by ultra-violet light in a few seconds, required to be treated with 1·188 grams of hydrogen peroxide per litre for three hours in order to become sterile. W. O. W.

The Kinetics of the Killing of Bacteria in Oxygen of Varying Concentrations and at Different Temperatures. THEODOR PAUL, GUSTAV BIRSTEIN, and ANTON REUSS (*Biochem. Zeitsch.*, 1910, **25**, 367—400).—The rate of death (disinfection rate) of dried bacteria (staphylococci) in oxygen-nitrogen mixture follows the equation of a unimolecular reaction, by means of which the constant for the rate of disinfection can be calculated. This constant is approximately proportional to the square-root of the oxygen concentration. The rate of death of staphylococci follows the same law as the slow oxidation of phosphorus. The temperature-coefficient of the disinfection rate is not constant, but increases with increasing temperature between 18° and 37°. The deviation of disinfection processes from Henry's law is attributable to the dissociation equilibrium of oxygen : $O_2 \rightleftarrows 2O$. Adsorption isotherms can also be employed to explain the deviation. The decrease of the temperature-coefficient of the disinfection rate also suggests the action of adsorption processes. The "garnet method" of Krönig and Paul for studying disinfection phenomena (*Zeitsch. Hyg. Infectk.*, 1897, **25**, 1) has proved itself of value in this research.
S. B. S.

Variability of the Proteolytic Power of the Anthrax Bacillus. JEAN BIELECKI (*Compt. rend.*, 1910, **150**, 1548—1550).—Successive cultures of anthrax bacillus taken from the same colony show gradually decreasing proteolytic activity, probably through inhibitory action of the peptone in the medium. In a medium containing no peptone, the proteolytic power shows little change with successive cultures, but increases if these are carried out alternately with peptone-containing and peptone-free solutions. The products of autolysis appear to stimulate diastatic activity, but new generations of the bacillus destroy the enzyme formed by the older ones. W. O. W

Determination of Volatile Acids in Fermentation Products of Certain Microbes by Duclaux's Method. G. SELIBER (*Compt. rend.*, 1910, **150**, 1267—1270).—With certain reservations the amount of volatile acids formed during putrefactive decomposition by bacteria is a characteristic of the particular bacillus present; especially is this the case with *B. butyricus*. Results in many cases, however, depend on the character of the medium; thus, to obtain constant values for *B. butyricus*, calcium carbonate must always be present.
W. O. W.

Emulsion Lævulan, the Product of the Action of Viscosaccharase on Sucrose. MARTINUS BEYERINCK [and D. C. J MINKMAN] (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **12**, 795—798. Compare this vol., i, 450).—Solutions of sucrose in tap water containing traces of potassium nitrate and phosphate inoculated with *B. mesentericus* (the common hay bacterium) change into a milk-white emulsion, and a thick, transparent slime layer is slowly formed at the bottom of the flasks. The lævulan formed is best precipitated with 50% alcohol, and, after dissolving in boiling water and again precipitating, is obtained as a colourless, nearly tasteless powder. This lævulan has $[\alpha]_D$ $-80°$ approximately; it is very strongly opalescent in solution, does not reduce Fehling's solution, and is not attached by alcoholic and lactic acid ferments, although decomposed by butyric acid ferments. Hydrolysis with boiling acids converts it into lævulose, the product having $[\alpha]_D$ $-70°$, or, after prolonged heating, $-64°$, which indicates partial destruction of the lævulose.

Hay bacteria produce no dextran at all; their cell wall consisting of lævulan. Other bacteria produce dextran, $[\alpha]_D$ $+132°$, alone from sucrose. The slimy cell-wall substances produced by various micro-organisms from dextrose, lævulose, and maltose are of a different nature from lævulan and dextran.

It is considered proved that lævulan and similar cell-wall substances are produced in consequence of the action of enzymes. E. F. A.

Influence of Concentration of Sucrose on the Paralysing Action of Certain Acids on Alcoholic Fermentation. M. ROSENBLATT and Mme. M. ROSENBLATT (*Compt. rend.*, 1910, **150**, 1363—1366. Compare Abstr., 1909, ii, 752).—The presence of sucrose diminishes the inhibitory effect of acids on fermentation, its efficiency in this respect increasing with concentration up to 12·5% of sucrose. The protective effect is most marked at those minimum concentrations of acid which in the absence of sucrose completely inhibit fermentation. In the case of acetic acid, for example, four times as much is required to inhibit fermentation in the presence of 10% of sucrose as when only 1·25% of this substance is present.

W. O. W.

Alcoholic Ferment of Yeast-Juice. V. Function of Phosphates in Alcoholic Fermentation. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1910, *B*, **82**, 321—330. Compare this vol., i, 292).—Addition of dextrose or lævulose to yeast-juice in presence of excess of phosphate results in a period of accelerated fermentation; 1 mol. of carbon dioxide is evolved for each mol. of sugar added.

When the available phosphate present is greatly reduced, the total fermentation is very small. Addition of small amounts of phosphate produces a relatively large increase in the total fermentation.

A hexosephosphate when digested with yeast-juice is hydrolysed by an enzyme, hexosephosphatase, with production of free phosphate and a sugar capable of being fermented by yeast.

In the chemical changes which the mol. of sugar may undergo in fermentation, 2 mols. of sugar are involved. N. H. J. M.

Influence of Nutrition on the Diastase Formation of Yeast. K. SAITO (*Woch. Brauerei*, 1910, 27, 181—183).—The tabulated results of experiments on the formation of diastase in cultures of *Aspergillus oryzae* under varying conditions of nutrition. As sources of nitrogen, peptone, tyrosine, leucine, alanine, asparagine, glycine, carbamide, ammonium tartrate, or ammonium oxalate were employed; whilst the carbohydrates were supplied by dextrose, lævulose, galactose, sucrose, maltose, lactose, and glycerol. In a second series of experiments the same sugars were employed in conjunction with inorganic nitrogen, such as ammonium salts of inorganic acids, potassium nitrate, or calcium nitrate. F. M. G. M.

Protein Formation in Ripening Seeds. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1910, 65, 431—476).—During the ripening of leguminous seeds, the percentage of proteins increases considerably, whilst the non-protein nitrogen diminishes. In the case of *Phaseolus vulgaris*, no absolute decrease of non-protein nitrogen was observed. Peas, however, showed a loss of non-protein nitrogen during ripening, although not great enough to account for the increase of proteins.

It is shown that the hulls of peas contain, in addition to considerable amounts of asparagine, small quantities of arginine, histidine, tryptophan, monamino-fatty acids, choline, and trigonelline, and that the same substances occur in the hulls of *Phaseolus vulgaris*. The non-protein nitrogenous compounds of the hulls are, therefore, very similar to those supplied to leguminous seedlings from the cotyledons.

Unlike the hulls, unripe pea seeds contain very little asparagine; they contain glutamine, which has not yet been detected in the hulls. It is suggested that asparagine migrates from the hulls to the seeds, where it is rapidly utilised for the production of proteins; that glutamine may also be present in the hulls, and that it passes into the seeds and accumulates there.

Milk-ripe wheat seeds contain only very small amounts of non-protein nitrogen. Monamino-fatty acids were found, and arginine seems to be present. No asparagine was found.

Attempts to detect in unripe seeds of peas and beans an enzyme which produces ammonia from asparagine were unsuccessful.

N. H. J. M.

Action of Some Hydrolysable Salts on the Higher Plants. ACH. GRÉGOIRE (*Bull. Soc. chim. Belg.*, 1910, 24, 200—209).—Rye plants were grown in cylinders containing nutrient salt solution, to each of which had been added a hydrolysable salt, formed from a strong base and a feeble acid. Those selected were calcium silico-humate, calcium carbonate, sodium-zeolite (analcime), and calcium zeolite (heulandite). Calcium silico-humate is unfavourable to the development of the rye plant; calcium carbonate slightly retards growth. Analcime causes six times as much growth as in its absence, and heulandite favours 59% more growth. The same relation is found in the amount of mineral matter taken up by the plants under the various conditions.

Rye has a great affinity for silicic acid, and the plants were found to have taken up a considerable quantity; in the case of the control solution and that containing calcium carbonate, this silica can only have been derived from the glass vessel. The zeolites cause a very considerable increase in the amount of silica in the plant, but this is not considered to have any influence on their action in facilitating growth.

In brief, the experiments indicate that hydrolysable salts, although themselves lacking any value as nutritive elements, have a specific influence on plant growth: this influence may be positive or negative according to the salt. E. F. A.

Assimilation of Free Atmospheric Nitrogen by Plants. EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 501—504).—The authors have cultivated a number of different cryptogams, phanerogams, and aquatic plants in closed vessels under sterile conditions, nutriment being supplied in the form of solutions free from nitrogen compounds. The results show that the assimilation of free nitrogen from the air is a general phenomenon with plants, which, however, vary considerably in their capacity for such assimilation. T. H. P.

Hairs of Stellaria Media and the Assimilation of Nitrogen by Plants. THOMAS JAMIESON (*Ber. deut. bot. Ges.*, 1910, **28**, 81—83).—A reply to Kny (this vol., ii, 443). Fairly large amounts of protein were detected in the club hairs by three usual methods, not described (compare Zemplen and Roth, *Erdészeti Kisérletek, Selmecbánya*, 1898, Heft 1—2; Jamieson, *Rep. Agric. Research Assoc.*, 1907–8). N. H. J. M.

Do Malt Infusions Contain Antidiastase? ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1910, **24**, 198—200).—A filtered infusion of green malt was divided into three parts, which were untreated, heated for thirty minutes at 55°, and heated for thirty minutes at 65° respectively. Tested by Lintner's method, the infusion heated at 55° had a slightly greater diastatic activity than the untreated infusion, but that heated at 65° was far less active. These facts are interpreted as indicating the presence of a small quantity of antidiastase approximately equal to the labile enzyme present. E. F. A.

Vernin (A Guanine Pentoside Occurring in Certain Plants). ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1910, **66**, 128—136).—This name is given to a nitrogenous substance isolated from young green plants of *Vicia sativa, Lupinus albus*, and *Trifolium pratense*, etiolated seedlings of *Cucurbita Pepo*, ripe seeds of *Lupinus luteus*, and *Arachis hypogaea*, unripe seeds of *Pisum sativum*, pollen of *Corylus avellana* and *Pinus sylvestris*, also in ergot. It occurs only in small quantity, and cannot always be detected, being apparently used up at some period subsequent to its formation. It is most conveniently prepared from etiolated seedlings of *Cucurbita Pepo* two and a-half to three weeks old.

The author assigns the formula $C_{10}H_{13}O_5N_5$. On hydrolysis with dilute sulphuric acid, vernin yields guanine and a pentose, which could not be identified because the initial quantity of material was so small, but was shown to be lævorotatory. Vernin is therefore a guanine pentoside. Its solubility in water is only 1 part in about 1320 at 17—18°, but it is more soluble in hot water. On cooling, it is deposited as fine needles or flat prisms, $C_{10}H_{13}O_5N_5,2H_2O$. A solution in $N/10$-sodium hydroxide was strongly lævorotatory; for a 2% solution, $[\alpha]_D$ at 20° = −60°; solutions in dilute sulphuric acid gave little or no rotation.

It is insoluble in absolute alcohol. Its aqueous solution is precipitated by phosphotungstic acid in presence of hydrochloric or sulphuric acids. Silver nitrate gives a transparent, yellow precipitate soluble in ammonia. Mercuric nitrate also gives a precipitate. Picric acid slowly throws down a picrate in aggregates of small crystals, brush-like or star-shaped under the microscope, melting at about 190°.

E. J. R.

Migration of Alkaloids in Grafts of Solanaciæ on Solanaciæ. MAURICE JAVILLIER (*Compt. rend.*, 1910, **150**, 1360—1363).—A number of cases of grafting have been examined in order to ascertain the extent to which migration of alkaloids takes place between the subject plant and the grafted portion. Negative results were obtained with grafts of *Belladonna* or tobacco on the potato plant, and with tobacco on tomato. A mixed graft of *Belladonna* on tomato gave physiological indications of migration, whilst in the inverse case more distinct evidence, both chemical and physiological, was obtained for the migration of mydriatic alkaloids. W. O. W.

Presence of Boron in Tunisian Wines. BERTAINCHAND and GAUVRY (*Ann. Chim. anal.*, 1910, **15**, 179—180).—The wines grown in the provinces of Bir-Kassa and Potinville (Tunis) were found to contain traces of boron as a natural constituent. L. DE K.

Presence of Tartaric Residues from Wine in an Antique Vase. GEORGES DENIGÈS (*Compt. rend.*, 1910, **150**, 1330—1331).—A vase dating from the first century A.D., discovered at Bordeaux, contained some coloured crystalline grains in which potassium hydrogen tartrate has been identified. W. O. W.

Composition of Milk Yielded by Cows Fed on Pasture Manured with Phosphates and Potash. JOHN GOLDING and SYDNEY G. PAINE (*Analyst*, 1910, **35**, 246—247).—Experiments showing that the use of superphosphate and potassium sulphate on a plot of poor soil used for pasturage, although increasing the quantity of milk yielded by the cows, had practically no effect on the non-fatty solids of the milk, not even on the mineral constituents thereof. The fat, however, showed a decided decrease. L. DE K.

Soil Solution. FRANK K. CAMERON (*J. Physical Chem.*, 1910, **14** 393—451).—The following subjects are discussed: (1) Absorption

by soils, including imbibition, the formation of solid solutions in the soil, and adsorption. (2) The relation of plant growth to concentration. (3) The balance between supply and removal of mineral plant nutrients. (4) The organic constituents of the soil solution, in which it is shown that the presence of organic dissolved substances in the nutrient medium produces effects on a growing plant of as great or even greater magnitude than those produced by inorganic dissolved substances. (5) Fertilisers. (6) Alkali, that is, the accumulation of soluble mineral substances at or near the surface of the soil under exceptional conditions of prolonged draught, a phenomenon which is pronouuced in arid and semi-arid regions.

T. S. P.

Fertilising Value of Rain Water. JOHANNES C. BRÜNNICH (*Ann. Rep. Dept. Agric. and Stock, Queensland*, 1908–9, 59—60. Compare von Feilitzen and Lugner, this vol., ii, 444).—Analyses of twenty samples of rain water collected at (1) Brisbane observatory; nineteen from (2) Bungeworgorai, Roma, and twelve from (3) Kamerunga, Cairns, North Queensland. The average amounts of nitrogen and the total amounts per acre for twelve months, corresponding approximately with 1908, were as follows:

	Rainfall, inches.	Nitrogen per million. as ammonia.	as nitrates.	Nitrogen per acre (lbs). as ammonia.	as nitrates.	Total.	% of total N. as ammonia.	as nitrates.
1.	45·44	0·216	0 186	2·228	1·920	4·148	53·7	46·3
2.	26·16	0·419	0·207	2·480	1·227	3·707	66·9	33·1
3	75·12	0·080	0·104	1·355	1·776	3·131	43·3	56·7

The total nitrogen per acre is very similar to the amounts recently found in other parts of the world, and does not seem to be influenced by the amount of rain. The relation of nitrogen as nitrates to total nitrogen, which is highest in the tropical rain at Cairns, is much lower than in New Zealand (compare Gray, *Proc. Austral. Assoc. Sydney*, 1888), where the amount of ammonia seems to be exceptionally low.

N. H. J. M.

Analytical Chemistry.

The Uses of Trichloroethylene in Analytical Chemistry. L. GOWING-SCOPES (*Analyst*, 1910, 35, 238—245).—Trichloroethylene, known in commerce as "Westrosol," is a colourless, readily volatile, and non-inflammable liquid, b. p. 88°. It dissolves practically all organic compounds that do not contain two or more carbonyl or hydroxyl groups, also some inorganic substances. It may be used for the extraction of fat in milk and similar products; the residue should be well rubbed with sand, and every trace of moisture be absent before extracting in the Soxhlet apparatus.

The solvent properties resemble those of chloroform and carbon tetrachloride. It withstands the action of alkalis, but being an unsaturated compound it cannot be employed in presence of oxidising agents. L. DE K.

Burette with Automatic Filling Arrangement. EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1910, **24**, 234—236).—The vertical stopcock of the burette is also connected with a siphon tube leading to the stock bottle containing the liquid used in the burette, and raised to a level such that the opening of the tube in the stock bottle is at the same level as the zero-mark of the burette. The stopper is bored in the ordinary way for connexion with the burette, but on the opposite side is a cavity of such a size that on turning the stopper through 180° from the position when the tap is open to the burette, connexion is made between the stock bottle and the burette. The latter then fills automatically. T. S. P.

An Adjustable Automatic Burette. J. D. ROSE (*J. Amer. Chem. Soc.*, 1910, **32**, 703—704).—Two tubes are connected at their lower ends by a four-way stopcock to the supply tube above and the delivery tube below. The stopcock is bored in such a manner that the exit of a hole is 90° from the entrance; 90° further around is the entrance of the other hole, which in turn is the same distance from its exit. Each passage can, therefore, be made to communicate with either side of the burette by simply turning the stopcock one-quarter turn to the right or left. The position of the hole permits the filling of one side and the emptying of the other simultaneously, so that while one charge is being delivered another is being measured.

The control of the liquid is secured by means of open floats containing a little mercury, which acts as a seal on the bottom of a glass tube; these tubes allow the passage of air to and from the burette. They are adjustable up and down, and permit of the calibration of the pipette in any desired quantities.

The liquid is taken from the supply bottle by means of a siphon or tubulature at the bottom. In either case a stopcock is interposed between the supply and the burette as a precaution. L. DE K.

Modification of Nowicki's Gas-absorption Pipette. LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1910, **24**, 233—234).—The bulb containing the spiral in Nowicki's apparatus (Abstr., 1905, ii, 760) has heen made shorter and wider, with the result that for the same length of spiral the inclination of each turn to the horizontal is considerably diminished. The gas thus passes more slowly through the spiral, and the absorbing effect is better. A subsidiary opening has also been provided towards the centre of the spiral, so that when the surface of the absorbing liquid falls below the top end of the spiral, the circulation of liquid will take place through this subsidiary opening. T. S. P.

Modification of the Winkler-Hempel Gas Burette. LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1910, **24**, 231—232).—The

modification is similar to that already described by Gwiggner (this vol., ii, 445), except that the capillary tube which puts the burette in connexion with the pipette is horizontal instead of vertical.

T. S. P.

Gas Analysis by Condensation. ERNST ERDMANN and H. STOLTZENBERG (*Ber.*, 1910, **43**, 1702—1707).—The method consists in submitting the gas to be analysed to such a temperature that one constituent is completely liquefied (or solidified). The uncondensed gas is then completely separated (for apparatus used, see succeeding abstract) and its volume measured. The condensed gas is allowed to vaporise, and its volume measured.

The method possesses the advantage that the constituents of the gaseous mixture are separated without being absorbed, and can be tested as to their purity. Moreover, it offers a check on the accuracy of working, since the sum of the volumes of the gaseous constituents must be equal to the volume of the original mixture. It can only be used, however, when the vapour pressure of the higher boiling constituent is negligible at the boiling point of the lower boiling constituent.

Accurate analyses of the following gaseous mixtures were made, the condensing agent being indicated in each case. Ethylene and hydrogen (liquid air, $-190°$); ethylene and oxygen, or air (liquid oxygen, $-182·7°$), the condensation of the ethylene being allowed to take place under slightly diminished pressure; carbon dioxide and oxygen (pentane bath at $-130°$); nitrous oxide and oxygen (pentane bath at $-155°$ to $-160°$).

T. S. P.

Apparatus for Gas Analysis by Condensation. H. STOLTZENBERG (*Ber.*, 1910, **43**, 1708—1710).—The apparatus consists essentially of three gas burettes and levelling tubes, similar in shape to the Hempel burettes, and a glass tube bent into the shape of a **Y**, so that the stem of the **Y**, which is bent into a number of **S**-shaped curves, can be immersed in the condensing liquid. The internal diameter of the tube is 1·5—2 mm. The gas to be analysed must be dry, and mercury is used as the measuring liquid.

Two burettes (*A* and *B*) are placed on one side of the condensing tube, and are so arranged that they may be used as a mercury pump for extracting and collecting uncondensed gas from the apparatus. The third burette (*C*) is placed on the other side of the condensing tube, and is used for measuring the gaseous mixture, and also the constituent gases.

The method of procedure is as follows: The gas to be analysed is measured in *C*, the remainder of the apparatus being full of mercury. It is then passed backwards and forwards through the condensing tube, which is immersed in the appropriate condensing liquid until condensation is complete, four such passages backwards and forwards being generally sufficient. The uncondensed gas is then pumped into *A*, the condensed gas allowed to vaporise, and forced into *C*, where it is measured, there being the necessary stopcocks for separating the various parts of the apparatus from each other. *C* is then emptied,

the uncondensed gas transferred to it from *A*, and its volume measured. T. S. P.

Estimation of Iodine in Protein Combinations. LOUIS W. RIGGS (*J. Amer. Chem. Soc.*, 1910, **32**, 692—698. Compare Abstr., 1909, ii, 504, 699).—A confirmation of the author's previous statement that in Baumann's process (fusion of the protein matter with sodium hydroxide and potassium nitrate) a little iodate is formed, which thus escapes detection. The acidified solution, after removing the iodine liberated with chloroform or, preferably, carbon tetrachloride, must, therefore, always be tested for iodine by Devarda's reduction process. L. DE K.

Estimation of Small Quantities of Iodine, with Special Reference to the Iodine Content of the Thyroid Gland. ANDREW HUNTER (*J. Biol. Chem.*, 1910, **7**, 321—350).—The material is fused with a mixture of anhydrous poatssium carbonate, anhydrous sodium carbonate, and potassium nitrate; the iodine is then estimated by Dupré's method, which consists in converting it quantitatively into iodic acid by the addition of chlorine water; the point at which the iodine is completely converted can be determined quite sharply by the disappearance of the starch or chloroform reaction. The method is stated to be more expeditious and accurate than Baumann's. W. D. H.

The Exact Estimation of Sulphur in Soluble Sulphates. EUGENE T. ALLEN and JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1910, **32**, 588—617).—To 350 c.c. of the solution containing about 1 gram of an alkali sulphate are added 2 c.c. of hydrochloric acid, and the liquid is heated to boiling. A sufficiency of barium chloride is now added at once, and the precipitate collected and treated as usual. Although the results are accurate, this is only caused by a compensation of errors. It is, therefore, better to precipitate the solution slowly by adding the barium chloride drop by drop at slight intervals, and to filter after the whole has remained for eighteen hours. The barium precipitate, after ignition, is not pure, and to get the correct weight, reference must be made to tables given in the original paper; the corrections vary according to the exact nature of the solution.

Barium sulphate may be freed from occluded alkali sulphate by dissolving in hot sulphuric acid and pouring the solution into water. The liquid contains the soluble sulphates, which may be recovered in the usual manner, and finally converted into barium sulphate. L. DE K.

Detection and Estimation of Sulphurous Acid in Wines. L. MATHIEU (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 1093—1096).—The presence of free and combined sulphurous acid in wine may be detected by treating 20 c.c. of the sample with about 1 gram of a mixture consisting of 4 grams of barium chloride, 20 grams of citric acid, and 100 grams of barium sulphate. After the lapse of about five minutes, the wine thus treated is filtered, and a few drops of

iodine solution are added to the clear filtrate. If free sulphurous acid is present, the filtrate becomes turbid, owing to the oxidation of the sulphurous acid, the resulting sulphuric acid combining with the excess of barium chloride in the solution. As little as 5 mg. of sulphurous acid per litre of wine yield a distinct turbidity. If the filtrate remains clear for five minutes after the addition of the iodine, heat is applied in order to oxidise the combined sulphurous acid which may be present, combined sulphurous acid not being oxidised readily by iodine at ordinary temperatures. Of course, if the wine contains free sulphurous acid, there will always be a certain amount of combined sulphurous acid present. The total sulphurous acid may be estimated by distilling a portion of the wine in an atmosphere of carbon dioxide, and collecting the distillate in a definite volume of standard iodine solution, the excess of iodine being then titrated with arsenious acid solution. Another portion of the wine is distilled in a similar way after the free sulphurous acid has been oxidised by the addition of iodine, followed by an addition of arsenious acid; the combined sulphurous acid is thus obtained in the distillate. The difference between the quantities of combined and total sulphurous acid found gives the amount of free sulphurous acid present. W. P. S.

Detection of Sulphuric and Phosphoric Acids in Wines. A. Hubert and F. Alba (*Ann. Chim. anal.*, 1910, **15**, 223—228).—Results of a series of experiments carried out by the authors show that plastered wines contain potassium hydrogen sulphate; the detection of the latter substance is, therefore, of little use as a means of distinguishing a plastered wine from one to which sulphuric acid has been added. Plastered wines contain more calcium sulphate and calcium tartrate than do normal wines and those containing sulphuric acid. It does not seem to be possible to distinguish between wines treated with calcium hydrogen phosphate and those to which phosphoric acid has been added. In both cases the alkalinity of the ash is diminished, calcium hydrogen phosphate possibly having slightly the greater effect in this direction. W. P. S.

Quantitative Distillation of Ammonia by Aeration. II. Philip A. Kober (*J. Amer. Chem. Soc.*, 1910, **32**, 689).—Further remarks on the apparatus described previously (Abstr., 1907, ii, 776), and a reply to criticisms.

The residue in the Kjeldahl flask is diluted with four volumes of ammonia-free water. When cold, the flask is connected with the absorption bottle, and, after reducing the rate of aeration, saturated alkali hydroxide is added in large excess, and the flask is shaken at the same time in a rotary fashion. The time required for the complete expulsion of the ammonia is at most three hours.

L. de K.

Estimation of Nitrogen as Ammonia. Ach. Grégoire (*Bull. Soc. chim. Belg.*, 1910, **24**, 221—223).—Instead of the usual method of distilling ammonia into excess of standard acid and titrating the excess of acid, the author recommends that the ammonia should be collected

in a special absorption apparatus, consisting of four bulbs containing distilled water, and then titrated directly with standard sulphuric acid. Indicators, such as methyl-orange, or even rosolic acid, then give a very sharp end-point. T. S. P.

Influence of Chlorine on the Estimation of Nitric Nitrogen. ROBERT STEWART and J. E. GREAVES (*J. Amer. Chem. Soc.*, 1910, **32**, 756—757).—It is already known that the estimation of nitrogen, existing as nitrates, by the phenolsulphonic acid method is affected by the presence of chlorides. In the course of an investigation of the influence of irrigating water on the movement and production of such nitrogen in the soil, a careful study of this question has been made. It has been found that when chlorine is present in as small a quantity as 2·638 parts per million, the estimation of nitric nitrogen gives low results, and that in the presence of larger amounts of chlorine, the results may be as much as 10% too low. E. G.

Estimation of Nitrites and Nitrates by the "Sulphophenol" Reagent. ISIDORE POUGET (*Bull. Soc. chim.*, 1910, [iv], **7**, 449—452). —Usually the Grandval and Lajoux process is used for the estimation of nitrates only, but it is known that the reagent (phenol dissolved in sulphuric acid) is affected by nitrites (compare Farcy, this vol., ii, 72), and it is now shown that the colour produced by a given quantity of nitrite is equivalent to that which would be produced by one-third the equivalent quantity of nitrogen, if this were present as nitrate.

Nitrites are decomposed by sulphuric acid in accordance with the equation: $3HNO_2 = 2NO + HNO_3 + H_2O$. Consequently, in applying the Grandval and Lajoux process to a mixture of nitrite and nitrate, the colour due to the nitrate is enhanced by that formed from the nitrite, and the quantity of nitrate originally present is given by the expression $N - n/3$, where N is the total nitrate found, and n the amount of nitrite, which must be determined previously.

A colorimeter with dipping prisms should be used for comparing tints, and a blue glass screen facilitates comparison. Chlorides, if present, should be eliminated by precipitation with silver sulphate before applying the process. If the original solution is dark coloured, due to organic matter, it may be cleared by means of freshly-precipitated lead oxide. The best results are obtained with liquids containing the equivalent of 0·03 to 0·3 milligram "nitric" nitrogen, the solution for comparison containing 0·1 milligram. T. A. H.

Estimation of Nitric Nitrogen as Ammonia. C. FRABOT (*Ann. Chim. anal.*, 1910, **15**, 219—223).—The author has investigated various reduction methods for the estimation of nitrates, and finds that simple reduction with aluminium in alkaline solution yields accurate results, and that the process recommended by Salle (this vol., ii, 451) is equally trustworthy. The method described by Pozzi-Escot (this vol., ii, 155) appears to be an unnecessary complication of the original aluminium process. W. P. S.

The Nitrogenous Substances Present in Bone Superphosphate. GASTON CHARDET (*Ann. Chim. anal.*, 1910, **15**, 215—219).— Nitrogen is present in bone superphosphate as humic nitrogen, amino-

nitrogen (glycine, leucine, alanine), basic nitrogen (arginine, lysine, histidine), ammonia, and in the form of undecomposed proteins. The latter are of less value as a manure than the humic substances, etc., and, as it is desirable to know in what proportions the various nitrogenous substances are present in superphosphate, the following methods are described for the estimation of the different groups. *Ammonia* is estimated by distilling the phosphate in the presence of magnesia. *Humic, basic, and amino-nitrogen.*—Fifty grams of the superphosphate are heated on a water-bath for thirty minutes with 150 c.c. of 90% alcohol and 15 c.c. of ammonia, the solution is then filtered, and the residue is washed with 250 c.c. of alcohol containing 5 c.c. of ammonia, the filtrate and washings being diluted with alcohol to a volume of 500 c.c. Two hundred c.c. of this solution are evaporated to expel the alcohol, the residual solution is treated with a slight excess of barium hydroxide, again boiled, and the precipitate formed is collected on a filter, washed with water, and the nitrogen is estimated in it by Kjeldahl's method; the quantity of nitrogen found represents the humic nitrogen. The filtrate from the barium hydroxide precipitate is acidified with hydrochloric acid and treated with phosphotungstic acid, which precipitates the basic nitrogenous substances present. The filtrate from the tungstic acid precipitate is evaporated, and the amino-substances are estimated in the residue by Kjeldahl's method. The residue remaining insoluble in ammoniacal alcohol contains the proteins, and the latter are estimated in a portion of the dried residue after the ammonia has been removed by boiling in the presence of magnesia. The following percentage quantities of nitrogen were found in four samples of bone superphosphate examined: total nitrogen, 0·78—2·10; ammoniacal nitrogen, 0·03—0·08; humic nitrogen, 0·04—0·11; basic nitrogen, 0·11—0·31; amino-nitrogen, 0·38—1·12; protein nitrogen, 0·18—0·48. W. P. S.

Gravimetric Estimation of Phosphates. A. H. MAUDE (*Chem News*, 1910, **101**, 341).—Woy's process (weighing as phosphomolybdic anhydride: Abstr., 1898, ii, 138) is recommended. L. DE K.

Estimation of Carbon in Steel by means of Allihn's Filter Tube. PRETTNER (*Chem. Zeit.*, 1910, **34**, 578—579).—The crude carbon is separated in the usual manner by boiling the steel with copper chloride, etc., and collected in an Allihn filter tube, which also serves as the combustion tube. After being dried at 110—120°, the carbon is burnt in a current of purified oxygen, and the carbon dioxide absorbed in Dennstedt's soda-lime apparatus. As, however, there is always formed a certain amount of carbon monoxide, the oxygen, after leaving the Allihn tube and traversing a calcium chloride tube, is passed through a 25—30 cm. long quartz tube filled with copper oxide spirals, and heated to redness. Two burners only are required, one for each tube. After leaving the absorption apparatus, the oxygen passes through a 60 cm. long rubber tube into a small bottle containing water, so as to be able to regulate the number of bubbles passing through. L. DE K.

The Mercury Cathode in Rapid Electro-analysis. W. S. KIMLEY (*J. Amer. Chem. Soc.*, 1910, **33**, 637—641).—In the process recommended by the author, the amalgam is formed and weighed in the same flask, as the transfer of the amalgam to a special weighing flask is sometimes attended with loss.

A platinum wire is sealed into the bottom of a round-bottomed flask holding about 125 c.c., and when 40 grams of mercury are introduced, the whole weighs about 65 grams. When the deposition is complete, the solution is siphoned off as far as possible without breaking the circuit, the flask is filled with water, and this is repeated until the current drops nearly to zero. The flask is then removed from the stirrer, and the liquid removed by a glass tube drawn out to a point and attached by a rubber tube to the suction tube of a filter pump. After thoroughly washing with water, and the last drops having been removed, the amalgam is washed with alcohol, then with ether, and the last traces of this are removed by placing the flask in a water-oven.

A convenient cell when dealing with a small volume of liquid is described. L. DE K.

The Filtrate from the Precipitate with Hydrogen Sulphide [in Qualitative Analysis]. JULIUS PETERSEN (*Zeitsch. anorg. Chem.*, 1910, **67**, 253—256).—An improved method of qualitative analysis after removal of the hydrogen sulphide precipitate. Barium and strontium are precipitated with sulphuric acid, and sodium carbonate, sodium sulphide, and sodium hydroxide are then added. The filtrate contains only aluminium. The residue is dissolved in hydrochloric acid to which a little sodium sulphide is added. Cobalt and nickel sulphides remain insoluble. The filtrate is boiled to remove hydrogen sulphide, and sodium carbonate and hydroxide are added. Only zinc goes into solution. The residue is treated with sodium peroxide, and heated momentarily to boiling. Chromium is thus removed as chromate. The residue is now dissolved in hot 5% acetic acid, containing 5% of sodium phosphate. Calcium and magnesium are dissolved, whilst iron and manganese remain insoluble. A shortened form of the scheme is applicable if cobalt, nickel, and chromium are known to be absent. C. H. D.

The Detection and Estimation of Very Small Quantities of Silver. G. STAFFORD WHITBY (*Zeitsch. anorg. Chem.*, 1910, **67**, 62—64).—Several organic compounds, such as sucrose, starch, dextrin, cellulose, and glycerol, yield a dark coloration with silver salts in presence of sodium hydroxide, owing to the formation of colloidal silver.

Fifty c.c. of the very dilute silver solution are taken, a few drops of a concentrated solution of sucrose are added, the beaker is placed in boiling water for two minutes, and, after adding 6 drops of $N/1$-sodium hydroxide, the heating is continued for twenty to thirty seconds. After cooling, the solution is transferred to a Nessler tube and compared with a standard. The quantity of silver that may be thus detected is 0·000002 gram in 50 c.c. The sensitiveness is equal to

that of the nephelometer (Richards and Wells, Abstr., 1904, ii, 287), and the reaction may thus be employed in atomic weight estimations. Ammonia must be absent, but copper, zinc, mercury, bismuth, cadmium, and lead are without influence if not present in sufficient quantity to yield visible precipitates with the alkali. C. H. D.

Rapid Estimation of Copper in Coarse Metal. Br. Winkler (*Chem. Zeit.*, 1910, **34**, 603).—One gram of the powdered sample is heated in a 100 c.c. flask with 10 c.c. of strong nitric acid and 10 c.c. of sulphuric acid on a sand-bath until sulphuric fumes appear. When cold, a little water is added, and the whole is heated until a clear solution is obtained. Any arsenic is oxidised by addition of 0·5 gram of potassium chlorate. The iron is precipitated by ammonia, and when cold the solution is diluted to the mark, shaken, and filtered. Fifty c.c. of the filtrate are then acidified with sulphuric acid, 3 grams of potassium iodide are added, and the liberated iodine is titrated with thiosulphate as usual; it is advisable to check this by means of pure metallic copper.

In the case of ores, 2 grams are taken and heated with 10 c.c. of nitric, 5 c.c. of hydrochloric, and 15 c.c. of sulphuric acid, and treated further as directed. L. de K.

Application of the "Aluminium Reaction" in the Analysis of Mercury Compounds. C. Reichard (*Pharm. Zentr.-h.*, 1910, **51**, 443—449).—Further particulars as to the corrosive action of soluble mercury salts on aluminium foil (formation of a characteristic stain of aluminium hydroxide: Abstr., 1907, ii, 691).

Free acids should be absent. Although the test is, as a rule, given by soluble salts only, there are exceptions, as mercuric iodide also gives the reaction; mercuric sulphide will cause a stain on aluminium if struck with a hammer, but in analytical practice it should be converted into the chloride.

The aluminium foil should be absolutely free from greasy matter; in this case the reaction is astonishingly delicate.

A mixture of dry mercuric chloride and copper, or cadmium sulphate, also causes the stain to appear, but in solutions containing these metals the test fails. L. de K.

Volumetric Estimation of Mercury in Galenical Preparations. R. Grüter (*Pharm. Zeit.*, 1910, **55**, 427—428).—The author describes the process used in the titration of mercuric chloride in the Neisser–Siebert lotion used for disinfecting purposes, which contains a large amount of colloidal matters.

45·16 Grams of the preparation are diluted with 250 c.c. of water, and introduced into a 750 c.c. stoppered flask. After shaking vigorously for a few minutes, a solution of 5 grams of potassium iodide is added, and the whole again shaken for ten minutes, when 50 c.c. of 10% sodium hydroxide and 20 c.c. of 40% formaldehyde are added. After shaking gently for ten minutes, 12 c.c. of glacial acetic acid are added, and then 15 c.c. of $N/10$-iodine. After again shaking for ten minutes, the excess of iodine is titrated with $N/10$-sodium thiosulphate.

Ten c.c. of $N/10$-iodine taken up represent 0·135 gram of mercuric chloride.

L. DE K.

The Estimation of Mercury in Urine and Fæces. CONRAD SIEBERT (*Biochem. Zeitsch.*, 1910, **25**, 328—332).—The organic matter is destroyed by the Neumann process, and the mercury precipitated as sulphide and weighed. The author gives full experimental details.

S. B. S.

Volumetric Estimation of Cerium in Cerite and Monazite. FLOYD J. METZGER and M. HEIDELBERGER (*J. Amer. Chem. Soc.*, 1910, **32**, 642—644).—An application of the process described by Metzger to the analysis of cerite and monazite (oxidation with sodium bismuthate, reduction of the ceric salt with ferrous sulphate, and titration of the excess of iron with standard permanganate: Abstr., 1909, ii, 626).

In the case of cerite, 0·5 gram of the finely-powdered sample is fused with potassium pyrosulphate, and the mass dissolved in 350 c.c. of water containing 5 c.c. of sulphuric acid. In the case of monazite, 0·6 gram of the sample is heated for six hours with sulphuric acid in a porcelain dish, and then poured into 350 c.c. of cold water. In either case the solution is filtered, heated to boiling, and mixed with 100 c.c. of saturated solution of oxalic acid. The precipitate formed, which includes the cerium, is then washed and treated as follows:

(1) It is washed off the filter with water, dissolved by means of 20 c.c. of sulphuric acid, 5 grams of ammonium sulphate are added, and, after diluting to 100 c.c., the liquid is boiled with sodium bismuthate as directed previously. This process gives satisfactory results if the amount of oxalates is but small; hardened filters are recommended.

(2) The filter containing the oxalates is burnt, finally over the blast lamp. The oxides are then heated with 10 c.c. of sulphuric acid, and when cold poured into 100 c.c. of water; if no solution takes place, another 10 c.c. of acid are added, and the liquid is heated until a clear yellow solution is obtained. After diluting to 100 c.c., 2 grams of ammonium sulphate are added, and oxidation is effected with 1 gram of sodium bismuthate.

(3) The oxalates are boiled with aqueous sodium hydroxide, and the washed precipitate is dissolved in dilute sulphuric acid and then treated as directed in (2). This method is by far the best.

L. DE K.

Eosin Reaction of Glass at Fractured Surfaces. II. FRANZ MYLIUS (*Zeitsch. anorg. Chem.*, 1910, **67**, 200—224. Compare Abstr., 1907, ii, 910).—The method of studying the "weathering" qualities of glass by means of iodoeosin has now been extended to the heavier optical glasses. A microchemical method of analysing such glasses quantitatively is described. The bases of glass absorb eosin from its ethereal solution, but silica or boric acid do not. Alumina has a slight action. Pure lead silicate absorbs slowly, basic silicate rapidly.

Long immersion of the heavier glasses in the solution causes

increased absorption which is not proportional to the weathering, but immersion for one minute in a solution containing 0·5 gram of iodoeosin per litre gives a true measure of the alkalinity of the glass. For weathering experiments, the glass is kept, with the fractured surface uppermost, in a vessel containing moist air. Under these conditions, the alkalinity of heavy glasses decreases during weathering, becoming constant after about a week. The values of the alkalinity for different glasses after this time are comparable with one another.

A concentrated solution of sodium silicate, mixed with lead oxide, sets to a hard mass. A more dilute solution yields a colloidal solution, which coagulates at 50°, and a similar solution is obtained from ignited silica, lead oxide, and a cold solution of sodium hydroxide. The action of water on lead glass consists in the formation of a concentrated solution, which contains all the constituents of the glass. Further addition of water causes hydrolysis and the formation of colloids, which then coagulate, depositing a layer of gelatinous silicates. The only portion of the glass which is then reactive towards iodoeosin is the alkali produced by hydrolysis, and converted into carbonate in the process of weathering. The decrease in alkalinity during weathering is greatest in glass containing a large proportion of lead oxide. The decrease is still more strongly marked in barium glasses, and is perceptible in zinc glass. The experiments are extended to twenty-five heavy glasses. The weathering increases with the amount of alkali, and is lessened by the presence of much baryta or zinc oxide. The replacement of silica by boric acid has little influence. Some alkaline borosilicate optical glasses weather to one thousand times the extent of stable heavy glasses.

Polished surfaces of glass require two years for a comparison of their weathering properties, and then give the same order of stability as is given by fractured surfaces in seven days. C. H. D.

The Estimation of Iron in Blood. D. Charnass (*Biochem. Zeitsch.*, 1910, **25**, 333—340).—For clinical purposes, Jolles' colorimetric iron thiocyanate method is applicable. The colour is not directly proportional to the amount of iron present. The author gives details as to the preparation of the colour scale, and of a colorimeter for employment in the estimations. S. B. S.

Electrolytic Separation of Nickel and Cobalt. Eugenio Piñerúa Alvarez (*Ann. Chim. anal.*, 1910, **14**, 169—170).—For the estimation of nickel only, the nickel cobaltocyanide formed by the action of potassium cyanide on nickel and cobalt sulphates in presence of sulphur dioxide (0·5 gram) is dissolved in a mixture of 100 c.c. of water and 10 c.c. of ammonia, D 0·927, and 5 grams of ammonium sulphate are added. When submitted to electrolysis for two hours in the cold, $D_{N}100 = 0{\cdot}40$ ampere and 3·7—4 volts; the liquid deposits the nickel in a brilliant film free from cobalt, but containing some partly-combined carbon.

To precipitate the two metals jointly, 1 gram of nickel cobaltocyanide is dissolved in 100 c.c. of water and 50 c.c. of ammonia, and,

after adding 10 grams of ammonium sulphate, the liquid is submitted to electrolysis for one hour at 50—60°; D_{N100} = at first, 1 ampere, towards the end 1·5 ampere and 3·8 volts. L. DE K.

New Volumetric Method for Cobalt and Nickel. GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1910, 32, 757—761).—A method is described for the volumetric estimation of cobalt and nickel by means of potassium ferrocyanide, which is of particular value for estimating nickel in steel.

A solution containing 20 grams of potassium ferrocyanide per litre is standardised against a cobalt or nickel solution of known strength. Three equal portions of the solution, each containing about 0·1 gram of the metal, are treated with 10 c.c. of 10% ferric chloride solution, 2—3 grams of citric acid, and a slight excess of ammonia. The solutions are then diluted to 100 c.c., and brought to a temperature of 65—75°. The ferrocyanide solution is added gradually with constant stirring, and nickel or cobalt ferrocyanide is precipitated. As the titration proceeds, a drop or two of the solution is transferred by a stirring rod to a paraffined white plate and acidified with a drop of dilute acetic acid. The solution is well stirred, and a second test made beside the first. The titration is continued until a greenish colour is developed in about five minutes at a definite point in the series. It is convenient to titrate the first portion roughly, and then to find the exact point with the other two portions. The method cannot be employed in presence of metals, such as copper, zinc, and manganese, which react with the ferrocyanide.

In order to estimate nickel in steel, 1 gram of borings is placed in a 150 c.c. flask, and 10—15 c.c. of dilute nitric acid are added. Potassium chlorate is added to the solution, which is then boiled until all the chlorine has been expelled. After repeating this treatment with potassium chlorate, the manganese dioxide is removed by filtration, and the nickel is estimated by the method already described.

The estimation of nickel in steel can also be accurately effected by the following method, which is based on those of Johnson (Abstr., 1907, ii, 819) and Campbell and Arthur (Abstr., 1908, ii, 779).

Steel borings (0·5 gram) are dissolved in nitric acid by the method described, and the solution is treated with 2—3 grams of citric acid, 2 grams of sodium pyrophosphate, and a slight excess of ammonia. The solution is diluted to 150 c.c., and cooled to 20°. A few drops of a 10% solution of potassium iodide are then added, and just sufficient *N*/10-silver nitrate to produce a distinct turbidity. Potassium cyanide solution, standardised by means of *N*/10-silver nitrate, is then slowly introduced with constant stirring until the turbidity just disappears and the solution becomes golden-yellow. If the solution remains bright for five minutes, the titration is complete.

This method is not applicable to solutions containing large amounts of cobalt, since a peculiar dark precipitate is produced during the titration which interferes with the end-reaction. E. G.

Estimation of Nickel in Nickel Steel. HERMANN GROSSMANN and B. SCHÜCK (*Analyst*, 1910, 35, 247—248).—Rhead (this vol., ii, 352)

has entirely overlooked the process recommended by the authors, to which they now once more call attention.

0·5—2 Grams of nickel steel are dissolved in *aqua regia*, and evaporated on the water-bath to a volume of 10 c.c. The solution is filtered, and 15 grams of sodium potassium tartrate added for each gram of steel used in the assay; should a precipitate form, it is dissolved by a little ammonia. In the presence of much manganese, oxidation is prevented by hydrazine sulphate. Ammonia and about 40 c.c. of 20% sodium hydroxide are added, and then a cold 10% solution of dicyanodiamidine sulphate. If but little nickel is present, the precipitation takes only a short time. The precipitate is filtered through a Gooch crucible, washed with cold ammoniacal water, dried at 120—130°, and weighed.

For rapid work, however, the titration with potassium cyanide is recommended (compare Campbell and Arthur, Abstr., 1908, ii, 779).

L. DE K.

Use of Silver in the Estimation of Molybdenum, Vanadium, Selenium, and Tellurium. CLAUDE C. PERKINS (*Amer. J. Sci.*, 1910, [iv], **29**, 540—542; *Zeitsch. anorg. Chem.*, 1910, **67**, 361—364. Compare Gooch and Perkins, Abstr., 1909, ii, 932).—It has been found that molybdenum, vanadium, selenium, and tellurium may be estimated by making use of the fact that the oxides of these elements liberate iodine from an acidified solution of potassium iodide. The reactions evolved may be represented by the equations: $2MoO_3 + 4KI + 4HCl = 2MoO_2I + 4KCl + 2H_2O + I_2$; $V_2O_5 + 2HCl + 2KI = V_2O_4 + 2KCl + H_2O + I_2$; $SeO_2 + 4KI + 4HCl = Se + 4KCl + 2H_2O + 2I_2$; $TeO_2 + 4KI + 4HCl = Te + 4KCl + 2H_2O + 2I_2$. The liberated iodine is estimated by shaking with specially prepared electrolytic silver in an atmosphere of hydrogen, and measuring the increase in weight of the silver. In the case of the oxides of selenium and tellurium, the increase in weight represents the iodine liberated plus the selenium or tellurium.

H. M. D.

Qualitative Test for Small Quantities of Gold and Silver. G. ARMANI and J. BARBONI (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 290—292).—It has been found that the production of coloured colloidal solutions of silver and gold by the reducing action of formaldehyde in alkaline solution can be used for the detection of very small quantities of these metals. The violet colour obtained with silver can still be recognised with certainty in the case of a solution containing 1 part of silver in 200,000 parts. The sensitiveness of the reaction in the case of gold is of the same order. If, however, the solution contains less than 1 part of gold in 100,000 parts, the violet colour is not developed until the solution is boiled. The tests are recommended for the detection of silver and gold on plated goods. In the case of plated copper or brass articles, these are treated with a mixture of 1 part of nitric and 9 parts of sulphuric acid, which removes silver, but has no action on copper or brass. In testing for gold, the material is treated with nitric acid, the insoluble residue is then digested with aqua regia, heated to dryness with sulphuric acid, and the residue dissolved in a small quantity of water.

H. M. D.

Oxidation of Organic Matter by Potassium Permanganate. EDMOND POPPE (*Bull. Soc. chim. Belg.*, 1910, **24**, 237—239).—In determining the organic matter present in water by the permanganate method, it is usual, according to the method of Kubel and Tiemann, to calculate the quantity of organic matter by multiplying the weight of permanganate used by five. The author tests this on aqueous solutions of thirteen organic compounds (various sugars, acids, etc.), and finds that the factor 5 is very far from correct. Moreover, the actual oxidising power of potassium permanganate in acid solution with respect to these organic substances is not equal to the theoretical. The temperature and time over which the experiments lasted are not stated. T. S. P.

Determination of the Source of Naphtha or its Derivatives. N. CHERCHEFFSKY (*Compt. rend.*, 1910, **150**, 1338—1341).—Naphtha is fractionated below 300° until one-twentieth of the volume has been collected, and the following constants determined in the distillate: (1) Density at 15°; (2) mean b. p.; (3) index of refraction; (4) solubility-coefficient; (5) iodine number; (6) temperature at which a hot alcoholic solution becomes turbid when cooled in a sealed tube; (7) temperature at which a hot mixture of the oil with acetic anhydride becomes turbid when cooled in an open tube. The author gives in tabular form the foregoing data for a number of naphthas from different localities, and states that they may be used to determine the origin of commercial naphthas, and to give some information as to their composition. W. O. W.

Estimation of Blood-Sugar. LEONOR MICHAELIS and PETER RONA (*Zeitsch. physiol. Chem.*, 1910, **67**, 104).—Remarks in reference to the paper by Bang, Lyttkens, and Sandgren (this vol., ii, 554), who have not given the present authors due credit for their work.
W. D. H.

The Most Simple Method for the Estimation of Dextrose in Urine. FRANZ LEHMANN (*Apoth. Zeit.*, 1910, No. 25. Reprint, 3 pp.).—A slight modification of the process described previously (Abstr., 1909, ii, 442), the clarification of the urine by means of basic lead, acetate, and sodium carbonate being omitted. After boiling with excess of Fehling's solution, the excess of copper is estimated by de Haen's iodometric process.

A convenient table is given to facilitate the calculation of the sugar content. L. DE K.

Analysis of Artificial Honey. F. MUTTELET (*Ann. Falsif.*, 1910, **3**, 206—207).—Artificial honey may be detected, even when mixed with natural honey, by means of Fiehe's test, which depends on the the red coloration produced when resorcinol in hydrochloric acid solution is allowed to act on β-hydroxy-δ-methylfurfuraldehyde; the latter substance is always present in small quantity in invert sugar which has been prepared by heating sucrose in the presence of an acid. In carrying out the test, the honey is shaken with ether, and the

ethereal extract is allowed to evaporate spontaneously in a china basin. The residue obtained is then treated with a few drops of the reagent (1 part of resorcinol dissolved in 100 parts of hydrochloric acid, D 1·19). The appearance of a distinct cherry-red coloration denotes the presence of invert sugar in the sample. Natural honey may yield a yellowish-orange coloration with the test. W. P. S.

Apparatus for the Estimation of Cellulose. ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1910, **24**, 217—221).—The authors describe a modification of Stift's apparatus (Abstr., 1896, ii, 79) for estimating cellulose in foodstuffs according to the method of Henneberg and Stohmann. The neck of a pear-shaped flask, open at both ends, is fitted into a Gooch crucible by means of rubber. The Gooch crucible is charged with quartz and a layer of asbestos fibre, and is fitted into a thistle funnel for convenience of filtration. The foodstuff to be analysed is treated in the pear-shaped flask with sulphuric acid and alkali in succession, the contents of the flask being heated by a jet of steam, and the asbestos in the crucible kept in position meanwhile by a glass ram-rod. During this treatment, filtration is prevented by attaching rubber rubing to the thistle funnel, and raising the end to an appropriate height. After the treatment is complete, filtration is allowed to take place at atmospheric pressure. The succeeding operations are carried out as usual.

Twelve estimations can be made in one day, whereas the old methods would have required at least four days; the results are satisfactory. T. S. P.

Estimation of the Volatile Acids in Wines by means of Bötticher's Apparatus. THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 484—486).—The Bötticher apparatus (Abstr., 1907, ii, 138) is recommended particularly in laboratories where the analysis of wines is not of frequent occurrence.

The addition of a few drops of oil free from acidity is a good device to prevent foaming during the distillation. L. DE K.

Quantitative Colorimetric Estimation of Small Quantities of Hydrocyanic Acid. ERNST BERL and MAX DELPY (*Ber.*, 1910, **43**, 1430—1431).—A method for the estimation of hydrogen cyanide in amounts ranging from 0·004 to 0·00004 gram per c.c.

The solution to be estimated is made alkaline with potassium hydroxide (1 : 1), a large excess being avoided, and then a solution of ferrous sulphate (1 : 30) containing oxide added, so that there are at least 2 mols. of ferrous sulphate to 1 mol. of hydrogen cyanide. The mixture is left for ten minutes at room-temperature, being well shaken from time to time, then boiled for two to fifteen minutes, cooled, and 10% hydrochloric acid added until acid. A precipitate of Prussian blue forms gradually. After five hours, if the original solution is colourless, the whole is made up to 100 c.c., well shaken, and the colour of the suspensions compared in a Krüss colorimeter with standards made from potassium cyanide solutions of known strength. When the

supernatant liquor is strongly coloured after the Prussian blue precipitate has settled, it is decanted off and replaced by water.

Very dilute cyanide solutions, for example, 0·00004 gram HCN per c.c., are first acidified, extracted with ether, and the ethereal extract shaken with a small quantity of potassium hydroxide solution, whereby a cyanide solution is obtained of such strength that the above method can be used. T. S. P.

Estimation of Tartaric Acid in Natural Products. CONSTANTIN BEYS (*Compt. rend.*, 1910, **150**, 1250—1251).—The following process is stated to give better results than any method hitherto described.

After heating for thirty minutes 1—2 grams of the substance with its own weight of 5% sulphuric acid, 5 volumes of alcohol are added and 10 volumes of ether. The precipitate is filtered off, and washed with alcohol and ether in the same proportions. The filtrate is neutralised with 90% alcoholic potassium hydroxide, and then treated with 5—10 c.c. of the same solution. After heating to 38° and cooling, the liquid *A* is decanted from the precipitate *B*, and acidified with glacial acetic acid; the potassium hydrogen tartrate which separates is washed with 96% alcohol. The precipitate *B* is brought into solution with 12—15 c.c. of hot water, and treated with 5 c.c. of acetic acid; after shaking for five minutes, alcohol is added in amount equal to 65% of the volume of liquid. The precipitate is washed successively with 65% and 96% alcohol, added to the precipitate from *A*, and the whole titrated according to Goldenberg's method (Abstr., 1908, ii, 237), using phenolphthalein as indicator. W. O. W.

Formaldehyde Titration of Amino-acids in Urines. HANS MALFATTI (*Zeitsch. physiol. Chem.*, 1910, **66**, 152—164. Compare Abstr., 1909, ii, 837).—The urine, after removing phosphates as directed in the author's previous paper, should be made neutral to phenolphthalein before starting the formaldehyde titration. The first change to very faint pink should be taken as the end-point. It is also pointed out that the process, although suitable for clinical purposes, is not sufficiently accurate for scientific work.

L. DE K.

Estimation of the Lecithin-content of Soja-oil. M. RIEGEL (*Pharm. Zeit.*, 1910, **55**, 428).—The author extracts the crude lecithin from lecithin containing preparations by means of boiling methyl alcohol, and in the residue left on evaporation the phosphoric anhydride is estimated in the usual way. This multiplied by 11·36 represents pure lecithin. Soja-oil was found to contain 0·15% of this substance. L. DE K.

Use of Urotropin for "Desulphurising" Wines and Musts. HENRI FONZES-DIACON (*Bull. Soc. chim.*, 1910, [iv], **7**, 389—390).—Urotropin having come into use for "desulphurising" treated wines, the reaction described by Denigès (this vol., ii, 357) has been recommended officially for the detection of formaldehyde in such wines.

The author has already suggested the estimation of ammonia liberated by magnesia from wines as an additional means of ascertaining whether urotropin has been added to them. Denigès' colour reaction is only satisfactory when care is taken to have enough sulphuric acid present. He also points out that in applying Blarez's reaction (*Bull. Soc. Pharm. Bord.*, February 1910), depending on the reddish colour given by formaldehyde with phenylhydrazine hydrochloride, care must be taken to use for the initial distillation a fairly large volume of wine, slightly acidified with sulphuric acid. If too much acid is used or the distillation is carried too far, some formaldehyde is formed by the action of the acid on components of the wine.

T. A. H.

Estimation of Aldehydes in Alcohol. Preparation of Standard Aldehyde Solution. LÉON RONNET (*Ann. Falsif.*, 1910, **3**, 205—206).—Standard aldehyde solution for use in the colorimetric estimation of aldehydes may be prepared from aldehyde-ammonia after the latter has been washed with ether and dried over sulphuric acid. The aldehyde-ammonia must not be dried under reduced pressure over sulphuric acid, as in this case it undergoes decomposition and is converted into ethylideneimine, which in turn polymerises to form a triple molecule. Pure acetaldehyde may also be prepared by distilling a mixture of paraldehyde and concentrated sulphuric acid.

W. P. S.

New Method for Estimating the Three Methylamines and Ammonia in Mixtures. JEAN BERTHEAUME (*Compt. rend.*, 1910, **150**, 1251—1253. Compare Abstr., 1908, ii, 742).—After criticising adversely Bresler's method (*Ann. Chim. anal.*, 1901, **6**, 28), the author gives details of a process based on the insolubility of ammonium chloride and methylamine hydrochloride in chloroform. These two salts are then estimated by Francois' method (Abstr., 1907, ii, 391, 503,), and the di- and tri-methylamine remaining in chloroform solution separated by taking advantage of the greater insolubility of tri-methylamine periodide in water. W. O. W.

A Modification of the Nitrometer for Estimating Urea. GUSTAV MOSSLER (*Chem. Zentr.*, 1910, i, 1180—1181; from *Zeitsch. allg. Österr. Apoth.-Ver.*, 1910, **48**, 1—3).—The flask for the evolution of nitrogen is connected with an improved form of nitrometer, in which the adjustment to zero before an experiment is performed by opening a tap, and the adjustment of levels after the nitrogen is collected, is automatic. The original paper contains tables for the calculation of the percentage of urea. C. H. D.

Rapid Estimation of Albumin in Urine. AUFRECHT (*Pharm. Zeit.*, 1910, **65**, 345—346).—The results obtained by the author's method (this vol., ii, 560) come nearer to the gravimetric estimations than those obtained by the ordinary Esbach method. It is advisable to make a comparative experiment with a solution containing a definite amount of albumin, and to note the time required for complete pre-

cipitation, as this differs according to the power of the centrifuge used.

Excess of urates may be removed previously by cooling. If the urine contains more than 0·5% of albumin, it should be diluted with a suitable quantity of water. L. DE K.

A New Method for Estimation of Fibrin Ferment and Fibrinogen in Body-fluids and Organs. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1910, **25**, 79—83).—For estimation of the fibrin ferment varying quantities of the liquid containing the ferment are diluted to a definite volume with 1% saline and mixed with 2 c.c. of magnesium sulphate plasma, prepared by Schmidt's method, and left in a series of test-tubes on ice for twenty-four hours. The amount of the ferment-containing liquid just necessary to produce coagulation is observed. The amount of fibrin ferment is expressed by the number of times this quantity is contained in 1 c.c. The fibrinogen is determined in a similar way, only in this case the amount of ferment-containing liquid is kept constant and the amount of plasma varied. A similar system is adopted for expressing the number of fibrinogen units present. S. B. S.

The Guaiacum Test for Blood, and a New Modification of the Same with Sodium Peroxide. BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Zeitsch. physiol. Chem.*, 1910, **65**, 511—512).—The delicacy of the guaiacum-turpentine test is much increased by the addition of alcohol; and if sodium peroxide is used instead of turpentine, this test for blood is the most delicate known.

W. D. H.

The Value of the Guaiacum Reaction for the Forensic Detection of Blood. J. KRATTER (*Chem. Zentr.*, 1910, i, 1458; from *Viertalsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 42—51).—The contradictory results obtained with the guaiacum test for blood are due to the non-observance of the requisite conditions of the reaction. The guaiacum tincture should be freshly prepared, the turpentine oil must be old, and the blood solution concentrated. To fulfil these conditions, the blood is not dissolved in water, but taken up on moistened filter paper. The spot is then moistened with the guaiacum tincture, and two or three drops of turpentine oil are added. A blue colour is produced with the blood. Old samples, however, give a bright cherry-red colour with guaiacum tincture alone, which is characteristic for blood, and this reaction is not destroyed by putrefaction. The reactions should only be employed as preliminary tests. S. B. S.

Hæmochromogen and its Crystals. KALMUS (*Chem. Zentr.*, 1910, i, 1458—1459; from *Viertalsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 57—64).—The preparation of hæmochromogen crystals from blood by means of pyridine and ammonium sulphide is a valuable test, but it is also given by other agents, such as the purple-yielding bacteria. From human blood, the hæmochromogen crystals form typical

slender needles, resembling those of hæmatin. Other bloods yield other forms of crystals, although no particular form could be identified as typical for the species of animal. The instability of the crystals is the only disadvantage compared with the hæmin crystals. The hæmochromogen crystals can be readily distinguished from rust and other substances, and their formation is not readily inhibited by foreign substances, as hæmin crystals are. They can, furthermore, be examined by the microspectroscope in the violet and ultra-violet parts of the spectrum. S. B. S.

Hæmochromogen Test. MITA (*Chem. Zentr.*, 1910, i, 1459; from *Viertalsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 64—66).—To avoid the inconvenience of the separation of sulphur when ammonium sulphide is employed in the hæmochromogen test, the author employs de Dominicis' 10% phenylhydrazine hydrate reagent. The crystals should be examined for double refraction. In the presence of organic matter, the blood should be first dissolved in water or acetic acid, and the solution allowed to evaporate at room-temperature. As regards the action of putrefaction or sunlight on the reaction, the hæmochromogen test is at least as trustworthy as the hæmatin test.
S. B. S.

A Reagent for the Detection of Blood-pigment and the Preparation of Hæmochromogen Crystals. LOCHTE (*Chem. Zentr.*, 1910, i, 459; from *Viertalsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 66—71).—The reagent employed consisted of 10 parts of sodium hydroxide, 40 parts of distilled water, and 50 parts of 80% alcohol containing 2 parts of pyridine and 2 parts of ammonium sulphide. Six to ten c.c. of this reagent are employed for a few drops of diluted blood solution. If the red hæmochromogen solution thus obtained is shaken with air, the wine-red colour becomes yellow or brownish-yellow, according to the amount of hæmatin formed. The hæmochromogen bands thereby disappear, and are replaced by the pale band of alkaline hæmatin. The solution then reddens again, and the hæmochromogen bands reappear. This colour change can be repeated an indefinite number of times. Hydrazine sulphate can be employed in the reagent instead of ammonium sulphide, but it can then be kept only for a short time without change. The best crystals are obtainable from fresh blood when the pyridine and ammonium sulphide are added simultaneously, especially when a few drops of alcohol are added previously to fresh blood. In doubtful cases the crystals should be examined microscopically. S. B. S.

Use of Benzidine for the Detection of Blood and its Application in Medico-Legal Practice. ERNST WALTER (*Deutsch. Med. Woch.*, 1910, No. 7. Reprint, 10 pp.).—The author recommends the substitution of the benzidine test for the old guaiacum test as being more decisive. Pastilles may be made containing 0·1 gram of benzidine and 0·1 gram of sodium perborate (preferable to hydrogen peroxide) and just before use such a pastille is dissolved in 10 c.c. of glacial acetic acid. The use of benzidine paper also proposed cannot be recommended. If a suspected

spot on an article of clothing, etc., is to be examined for blood, it is moistened with a drop of physiological salt solution and well rubbed with a glass rod. The drop is then absorbed in a small piece of cotton wool free from fat, and the spot at once treated with a few drops of the reagent. In presence of blood a blue coloration is noticed.

L. DE K.

Use of Various Zinc Salts in the Detection of Urobilin. R. WEITZ (*J. Pharm. Chim.*, 1910, [vii], 1, 533—538).—Various authors have drawn attention to the green fluorescence produced in urines containing urobilin by the addition of zinc salts (Denigès, Abstr., 1908, i, 343, ii, 200; Roman and Delluc, Abstr., 1900, ii, 700), and have suggested this reaction as a means of detecting this substance. The author finds the following method of operating gives good results. The urine (20 c.c.) is mixed with zinc acetate (4 grams), alcohol (20 c.c.) of 95° strength is added, and the mixture shaken and filtered. The filtrate shows a marked green fluorescence if urobilin is present. The delicacy of the reaction is increased if the mixture is left from one to two hours before filtration. To liberate urobilin from the chromogen, which precedes it, the urine must be treated with a few drops of an oxidising agent, such as Gram's iodine solution, or alkaline permanganate. Mercuric sulphate should not be used as a defæcating agent before applying the test, as urobilin is liable to be lost in that way. Zinc lactate or valerate gives as good results as the acetate, but the basic carbonate is a little less delicate. Zinc sulphate or chloride may be used if their solutions are first made neutral by adding ammonia solution. Blood and biliary pigments do not interfere with this reaction, and can themselves be detected by the ordinary tests. If indoxyl is present, the urobilin should be separated by adding basic lead acetate solution, suspending the washed precipitate in alcohol, and decomposing it with dilute sulphuric acid, thus forming an alcoholic solution of urobilin to which, after exact neutralisation by ammonia, the test may be applied.

T. A. H.

The Detection of Peptolytic Enzymes in Animal and Vegetable Tissues. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1910, 66, 137—139).—An easy method for the detection of peptolytic enzymes consists in placing sections of the tissue in solutions of silk-peptone; after a few hours' digestion tyrosine crystals are found adhering to the sections if a peptolytic enzyme is present. Possibly the injection of the silk peptone into the organ and subsequent examination of it may throw light on the question as to what cells are concerned in the formation of the enzyme, and differences may be found in normal and pathological conditions. The enzymes in question were found in all the animal and vegetable tissues examined; in muscle, the amount as judged by the yield of tyrosine is small. The method may be used in plants to determine the date when such enzymes appear during germination. Another microchemical reaction which gives good results is to use polypeptides which contain tryptophan; the violet reaction with bromine water does not occur until tryptophan is liberated.

W. D. H.

Comparison of Results Given by Acidity Determinations and by Catalasimetry in Estimating the Freshness of Milk. J. SARTHOU (*J. Pharm. Chim.*, 1910, [vii], 1, 387—393).—Soxhlet's observation that milk only undergoes lactic fermentation after a period of incubation, is confirmed. In a series of trials with milks kept in the laboratory, it was found that the acidity remained constant during the first forty-two hours, whilst catalytic action on hydrogen peroxide increased, indicating that richness in bacteria increased, but that no acid fermentation of lactose occurred (this vol., ii, 326) during this period. The increase in catalytic activity of milk varies with the race of lactic bacillus it contains, and is much more marked for milk kept in a dairy than for milk kept in the laboratory. Further, the catalytic activity increased more rapidly in milk kept warm than in milk preserved at about 10°. T. A. H.

Estimation of Diastase in Milk. C. J. KONING (*Chem. Weekblad*, 1910, 7, 377. Compare van Haarst, *Chem. Weekblad*, 1910, 7, 354—355).—A reply to van Haarst's statement that Koning's method for estimating diastase in milk is useless. A. J. W.

Estimation of Diastase in Milk. J. VAN HAARST (*Chem. Weekblad*, 1910, 7, 391).—Polemical. A reply to Koning (preceding abstract). A. J. W.

The Apparent Diastase Reaction of Water on Starch. C. J. KONING (*Chem. Weekblad*, 1910, 7, 484—485. Compare preceding abstracts).—A reply to van Haarst, maintaining that the author's method of estimating diastase in milk is trustworthy. A. J. W.

Analysis of Gastric Juice. ALFREDO E. TAMAYO (*Ann. Chim. anal.*, 1910, 14, 172—173).—*Estimation of Pepsin.*—A solution is made containing 2 grams of pure albumin in 100 c.c. of water, and 0·8 c.c. of hydrochloric acid is added. Ten c.c. of this are added to 10 c.c. of the gastric juice contained in a test-tube; in a similar test-tube are introduced 10 c.c. of the albumin solution and 10 c.c. of water, and both tubes are then placed in a bath at 37° for an hour. The contents of the tubes are then transferred to two Esbach tubes up to the mark *U* and then diluted with dilute nitric acid (20 vol.%) up to the mark *R*. After some time, the volumes of the respective albumin deposits are read off, and the difference represents albumin acted on by the gastric juice.

Total Acidity and Organic Chlorine.—To 10 c.c. of the filtered sample are added three or four drops of strong alcoholic solution of phenolphthalein, and $N/10$-sodium hydroxide is added from a burette until a permanent rose colour is noticed. The liquid is then put into a flat porcelain dish and evaporated to dryness. The residue is heated to redness, and, when cold, the ash is moistened with a little water, and a volume of $N/10$-sulphuric acid equal to that of the alkali (X) used is added. After boiling to expel carbon dioxide, the excess of acidity is titrated with $N/10$-sodium hydroxide; the number of c.c. (x) used represents the hydrochloric acid, $X - x$ represents the organic acidity. On subtracting from x the figure found for free hydrochloric acid, the organic chlorine is found.

Estimation of Total Chlorine.—Ten c.c. of the gastric juice are mixed with an excess of sodium carbonate, and, after evaporating to dryness, the residue is ignited. The ash is dissolved in water, and the chlorine titrated as usual.

Estimation of Free Hydrochloric Acid.—Ten c.c. of the sample are titrated with $N/10$-sodium hydroxide until a drop of the liquid gives no longer the Gunzburg reaction on a warm porcelain slab.

The mineral chlorine is found by deducting from the total chlorine the chlorine existing as free hydrochloric acid and in organic combination. L. DE K.

Rapid Detection of Emulsin. E. FRANKLAND ARMSTRONG (*Proc. physiol. Soc.*, 1910, xxxiii; *J. Physiol.*, 40).—The term emulsin is used for the mixture of enzymes discovered in almonds by Liebig and Wöhler. The material to be tested is incubated with water for twenty-four hours in a corked tube, in the neck of which a piece of moistened Grignard's sodium picrate paper is suspended. As long as the paper remains orange, hydrogen cyanide is absent. A solution of amygdalin, phaseolunatin, or other cyanophoric glucoside is added, and the tube again incubated. If emulsin is present, hydrogen cyanide is rapidly produced, and the paper becomes coloured red; the speed of the change is a rough measure of the proportion of enzyme present. W. D. H.

Is there Caramelisation in Rivas' Test? DAVID W. HORN (*Amer. J. Pharm.*, 1910, 82, 151—161).—It is contended that the assumption sometimes made that the development of a brown colour (1) in old official "syrup of ferrous iodide," (2) when lactose is heated with sodium hydroxide, as in Rivas' test for *Bacterium Coli*, is due to the formation of caramel, is inaccurate. It is found that the optical rotation of dextrose is destroyed by heating with alkalis, that the brown colour formed in this reaction disappears on the addition of acids, and that it is also removed by passing oxygen through the solution. In the last respect the brown colour differs from that due to caramel. From information already on record regarding the action of alkalis on dextrose, it appears likely that a sodium dextrose compound is first formed, and that on further heating, organic acids and resin are produced. The lactose in Rivas' test, and the sucrose in the ferrous iodide syrup, may be supposed to break up, yielding dextrose, which might then condense to coloured substances, as described above. T. A. H.

General and Physical Chemistry.

Calculation of Optico-chemical Constants. H. STANLEY REDGROVE (*Chem. News*, 1910, **102**, 3—6, 14—15).—The method already employed in calculating thermochemical constants (compare Abstr., 1907, ii, 446, 604, etc.), in which the influence of the ethane and certain other links usually ignored is taken into account, is now applied to the experimental data for the refractive indices of aliphatic hydrocarbons. The molecular refractivities of these hydrocarbons for the a- and γ-hydrogen lines, calculated with the help of the "fundamental constants," are tabulated, and are shown to be in good agreement with the experimental values. The observed and calculated molecular dispersions are also in satisfactory agreement, but the results are less trustworthy, as the measurements are greatly affected by experimental errors. It is shown that the molecular dispersion of any hydrocarbon can be calculated by multiplying the number of ethane links in it by 0·13, the number of ethene (double) links by 0·32, and the number of ethine (triple) links by 0·28. The latter constant, however, is somewhat uncertain, owing to the scanty experimental data.

Brühl's method of calculating optico-chemical constants is open to objection, not only because certain links are not taken into account, but also because his constants are in some cases based on the assumption that aldehydes and ketones contain carbonyl oxygen only, whereas they are often equilibrium mixtures of enolic and ketonic forms.

G. S.

Production of the Fundamental Spectra of Potassium, Rubidium, and Cæsium. EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1910, **12**, 426—443; *Physikal. Zeitsch.*, 1910, **11**, 560—568. Compare Abstr., 1907, ii, 725; 1909, ii, 2).—The method described previously for the production of well-developed line spectra of the alkali metals and the halogens has been applied to the examination of alkali-metal fluorides. With suitable condensers placed in parallel with the discharge tube, line spectra of the halogens are obtained in the case of chlorides, bromides, and iodides. Fluorides, however, do not give the corresponding spectrum of fluorine, but under these conditions the so-called "fundamental spectra" of the alkali metals are developed. These spectra are characterised by the fact that the individual lines cannot be represented by any of the usual series formulæ. As the intensity of the condenser discharge increases, the series spectrum of potassium is gradually obliterated, and is replaced by the non-series "fundamental spectrum."

"Fundamental spectra" of rubidium and cæsium can be obtained in a similar way. As compared with potassium, the only difference exhibited by these metals lies in the fact that the conditions requisite for producing the two independent spectra are not so sharply differentiated in the case of rubidium and cæsium. H. M. D.

Spectra of Bismuth. WILHELM SCHWETZ (*Zeitsch. wiss. Photochem.*, 1910, **8**, 301—315).—The spark, arc, and flame spectra of bismuth have been examined. From his own and previous observations, the author draws the conclusion that the flame spectrum of metallic bismuth is free from bands, and is characterised principally by the blue line $\lambda = 4722$. The feebly-developed bands which are observed in the examination of bismuth salts are attributable to bismuth oxide. This band spectrum is also obtained in the case of bismuth chloride.

The spark and arc spectra are contrasted, and observations relating to the influence of pressure, self-induction, and a magnetic field on the spectrum are recorded. H. M. D.

Arc Spectrum of Zirconium. ALBERT BACHEM (*Zeitsch. wiss. Photochem.*, 1910, **8**, 316—332).—Detailed measurements have been made of the wave-lengths and relative intensities of the lines in the arc spectrum of zirconium between the limits $\lambda = 2166$ and $\lambda = 7169$. The wave-length measurements are based on the values of Buisson and Fabry for the normal lines of iron. H. M. D.

Connexion between Band Spectrum and Chemical Dissociation. JOHANN G. KOENIGSBERGER and K. KUPFERER (*Physikal. Zeitsch.*, 1910, **11**, 568—571).—Of the three types of absorption spectra which are exhibited by gaseous substances, the authors attribute the discontinuous band spectrum to intramolecular or intra-atomic conditions which are brought about by the process of chemical dissociation. Substances like iodine, bromine, sulphur, and selenium, the molecules of which undergo dissociation when the temperature is raised, exhibit a discontinuous band spectrum when the conditions are such that both undissociated and dissociated molecules are present in appreciable proportions. If by altering the conditions of temperature and pressure, one set of molecules is caused to disappear more or less completely, the substance in question will no longer give the discontinuous band spectrum. H. M. D.

Extreme Red and Infra-red Band Spectra of Carbonated Gases. F. CROZE (*Compt. rend.*, 1910, **150**, 1672—1673).—The spectrum of carbon monoxide consists of fourteen visible bands and a number of ultra-violet bands, the principal lines of which obey Deslandres' law. The author has photographed five bands of the same series in the infra-red, in which the wave-lengths of the headlines are 722·5, 747·2, 792·5, 836·8, and 881·0$\mu\mu$.

The cyanogen spectrum consists of two series of bands, the first extending from 4607$\mu\mu$ into the ultra-violet, and the second composed, according to Thalen, of thirteen bands between 7102$\mu\mu$ and 5245$\mu\mu$. This series extends into the infra-red, the headlines of the bands observed being 725·4, 740·0, 753·6, 800·1, and 813·4$\mu\mu$, whilst beyond these bands a very feeble continuous spectrum appears. An exposure of six to eight hours was necessary, and during this time fresh cyanogen was constantly circulated through the Geissler tube at 2 mm. pressure to prevent the appearance of the nitrogen bands.

Carbonated gases give the above two spectra and also Swan's spectrum, usually attributed to hydrocarbons or carbon. Bergmann has recently mapped the spectrum of the carbon arc between $640\mu\mu$ and $1400\mu\mu$, but the bands grade off in the opposite direction to Swan's. The author has photographed Bergmann's spectrum of the arc directly both in air and in a vacuum. R. J. C.

The Band Spectrum Obtained by Introduction of Manganous Chloride into the Oxygen Coal-gas Blow-pipe Flame. HERMANN CASARETTO (*Zeitsch. wiss. Photochem.*, 1910, **8**, 381—404).—Measurements of the band-spectrum were made between $\lambda = 4402{\cdot}4$ and $\lambda = 6707{\cdot}6$. The photographic records indicate that in this region there are ten similarly constituted groups of bands which fade away towards the red end of the spectrum. It is shown that the frequencies of the constituent bands of the respective groups are related to one another, and that the frequencies of corresponding bands of the several groups show differences which are very nearly constant.

The same band spectrum is obtained with other compounds of manganese, but the bands are more clearly developed in the case of the chloride. This leads the author to infer that the band spectrum is due to the metal itself. H. M. D.

Conditions Under which the Band Spectrum Attributed to Cyanogen may Appear. ANTOINE DE GRAMONT and DRECQ (*Compt. rend.*, 1910, **150**, 1235—1236).—The spectrum of sodium carbonate, or of sodium bromide or chloride containing 0·5% of carbon as carbonate, obtained by the use of a spark sufficiently powerful in itself to fuse the salts, showed all the characteristic bands of cyanogen. The salts were free from cyanide, and the conditions such that any cyanogen formed from the carbon and atmospheric nitrogen would be immediately decomposed, since, according to Andrews and Tait, cyanogen is decomposed into its elements by the electric spark. It is suggested that the spectrum usually attributed to cyanogen is merely the spectrum of a mixture of carbon and nitrogen. The bearing of this theorem on the question of the toxicity of Halley's Comet is discussed. R. J. C.

Three-fold Emission Spectra of Solid Aromatic Compounds. EUGEN GOLDSTEIN (*Brit. Assoc. Rep.*, 1909, 129—131. Compare this vol., ii, 469).—An aromatic substance, when cooled in liquid air and submitted to the action of cathode rays, does not, as was originally supposed (Abstr., 1904, ii, 689, 690), emit only a single spectrum. For each substance there appear three spectra, (*a*) the *initial spectrum*, (*b*) the *chief spectrum*, and (*c*) the *solution spectrum*. The first appears at the moment when the cathode rays fall upon the substance; its brightness diminishes and ultimately becomes very small, but it never entirely disappears. The light belonging to the initial spectra for colourless substances is always blue. The initial spectra begin in the red, but extend through the green aud blue into the ultra-violet; for two substances they are similar in general appearance, but never identical. The chief spectrum appears and grows brighter whilst the intensity of the initial spectrum is diminishing. In a large number

of cases it is so characteristic that it can be employed as a means of identification, even of isomeric compounds. The chief spectra always begin from the infra-red and end in the green or blue, or in some instances in the yellow.

The solution spectrum, which differs entirely from the others, appears when the aromatic substance is dissolved in a solvent and the solidified solution exposed to cathode rays. Whilst isomeric substances exhibit quite distinct solution spectra, the same substance emits different solution spectra when dissolved in different, even if isomeric, solvents. The light of the chief spectra is fluorescent, but that of the solution spectra is phosphorescent. E. H.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Report*, 1909, 135—141).—This report summarises the evidence showing that the presence or absence of a band in the absorption spectrum of a camphor derivative is independent of the occurrence of isomeric change. The catalytic action of impurities on the phenomena of colour, fluorescence and triboluminescence, and the relation of crystallisation to phosphorescence, fluorescence, and colour, are considered. E. H.

Absorption and Fluorescence of Rubidium Vapour. TAYLOR S. CARTER (*Physikal. Zeitsch.*, 1910, 11, 632—633).—When white light is allowed to fall on the vapour of metallic rubidium, it emits a well-developed, red-coloured, fluorescent beam of rays. Photographic records show that the fluorescence spectrum is discontinuous. The banded absorption spectrum, which determines the nature of the fluorescence, is found to be closely similar to the absorption spectra of potassium and sodium. H. M. D.

Magnetic Rotation of the Plane of Polarisation in Crystalline Liquid Substances. GERHARD VIETH (*Physikal. Zeitsch.*, 1910, 11, 526—527).—Measurements of the rotation of the plane of polarisation by the active amyl anisylideneamino-α-methylcinnamate in a magnetic field have shown that the rotations produced with oppositely directed fields are unequal. For yellow light, the dextro-rotation is about 6·3 times as large as the lævo-rotation; for green light, the ratio of the two rotations is only about 1·75. In all cases the rotation increases in proportion to the intensity of the magnetic field. H. M. D

The Transmission of β-Rays. J. ARNOLD CROWTHER (*Proc. Camb. Phil. Soc.*, 1910, 15, 442—458).—Experiments were carried out on the velocity and absorption of a beam of β-rays of radium rendered nearly homogeneous by passage through a circular arc in a uniform magnetic field, after the manner employed by W. Wilson (*Proc. Roy. Soc.*, 1909, *A*, 82, 612), except that a vacuum was employed to avoid the scattering of the rays by air while in the magnetic field. It was shown by the use of two similar arrangements, in which the magnetic field of the first was kept constant while that of the second was varied, that the velocity of the rays transmitted by a single arrangement did not vary

more than 1% from the mean value. The introduction of an absorbing sheet of aluminium (0·047 cm. thick) between the two arrangements caused a small but decided reduction in the velocity of the rays transmitted [from 2·735 ($\times 10^{10}$ cm./sec.) to 2·690 in one case, and from 2·903 to 2·881 in another]. In the first case, for the softer rays, the screen caused a reduction of 71%, and in the second case of 52% of the radiation, showing that the absorption is not due to any important extent to simple retardation. Glass behaved similarly to aluminium, but platinum was different, the beam, initially homogeneous, emerging with considerable range of velocity in either direction, but particularly in that of retardation. The law of absorption of these homogeneous β-rays was studied for aluminium and platinum. For the former the curve was neither exponential nor linear, but for the latter it was, after a slight initial steeper part, strictly exponential. The latter result is ascribed to the complete conversion of the rays into secondary rays in the first 0·001 cm. of platinum traversed. The analogy between the exponential absorption of these secondary β-rays and of secondary homogeneous X-rays is pointed out. F. S.

Relationships in the Emission of β-Rays and the Absorption of these by Matter. OTTO HAHN (*Ber. Deut. physikal. Ges.*, 1910, **12**, 468—474).—The deviability of β-rays by a magnetic field has been investigated by means of their action on a photographic plate. The photographic record obtained in the case of the β-rays emitted by the active deposit of thorium shows two very distinct bands, corresponding with the emission of two types of β-rays. These are the rays emitted by thorium-A and thorium-D respectively. Three other feebly-developed bands are also recognisable, and it appears therefore that the active deposit of thorium emits five different sets of β-rays.

When examined in the same way, radium-E_2 was found to give homogeneous β-rays. On the other hand, mesothorium-2 appears to emit at least six kinds of β-rays, and the photographic record obtained in the investigation of thorium-X shows that this also emits β-rays.

None of these substances gave a continuous β-ray spectrum, and the apparently continuous spectrum obtained by previous observers in the case of radium is attributed to the overlapping of a large number of independent bands. H. M. D.

The Structure of γ-Rays. EDGAR MEYER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, **32**, 647—662; *Jahrb. Radioaktiv. Elektronik.*, 1910, **7**, 279—295. Compare von Schweidler, this vol., ii, 376).—If the γ-rays were propagated as spherical waves from their origin, the von Schweidler variation due to the individual atomic disintegrations would not be altered by narrowing the cone of rays under investigation, but on the newer alternative view that the γ-rays are propagated along lines [as discrete particles (Bragg), energy-bundles (Einstein, Stark), or localised in ether-patches (J. J. Thomson)], a second von Schweidler variation of intensity would be superimposed, due to the heterogeneous structure of the "wave-front," and this would come into evidence the more as the pencil of rays is narrowed. The von Schweidler variations with a radium γ-ray source at the centre of a

hemispherical ionisation chamber were observed when the angle of the rays was diminished from 2π by lead screens. In several series of experiments the results were in agreement with the second hypothesis, and were incompatible with the first. The relative values of the variation for wide and narrow cones of rays were in good agreement with the results to be expected on the second hypothesis, calculated from the theory as developed by von Schweidler and K. W. F. Kohlrausch. It was proved in separate experiments that the results could not be due to variation of the ionisation of the gas, or of the secondary rays emitted from the walls of the ionisation chamber, for when these factors were varied, the character of the phenomena was not essentially altered. About 30,000 observations were made, and the error is estimated at about 10%, but the conclusion is clearly in favour of the rays being strongly anisotropic in structure, although whether they are propagated along lines or along narrow cones, widening as the distance from the origin is increased, is not apparent from these experiments. F. S.

Secondary Röntgen Rays from Metallic Salts. J. L. GLASSON (*Proc. Camb. Phil. Soc.*, 1910, **15**, 437—441).—The question examined was whether the nature of the characteristic homogeneous secondary *X*-radiation, produced when an element of atomic weight greater than 40 is subjected to *X*-rays (Barkla), was affected by the state of chemical combination of the element. The results with various salts of iron showed that even when the iron in the molecule is only one-sixth of the whole mass, and is, moreover, in the acid radicle (as in ammonium ferrocyanide), the radiation is mainly the homogeneous iron radiation, the light elements producing only a very small proportion of scattered primary radiation, which is considerably more penetrating than the secondary, and so comes into evidence only when the intensity is greatly reduced by absorption screens. The value of the absorption-coefficient for aluminium for the secondary *X*-radiation characteristic of any metal can be determined quite well by the use of its salts, and for manganese was found to be 100, by using manganese sulphate, which agrees with that predicted from its atomic weight.

F. S.

The Production of Cathode Particles by Homogeneous Rontgen Radiations. R. T. BEATTY (*Proc. Camb. Phil. Soc.*, 1910, **15**, 416—422).—Radiators of iron, copper, zinc, arsenic, and tin were subjected to primary *X*-radiation, and the homogeneous secondary *X*-radiations produced were (1) measured by means of an electroscope, and (2) received in a second ionisation chamber, through a parchment window covered with silver leaf, in which the air-pressure could be varied. The object was to investigate the absorption-coefficients (λ) of the cathode radiations produced by the secondary *X*-radiations in air and hydrogen. The latter produce an ionisation proportional to the pressure which can be subtracted from the total ionisation, the part due to the cathode radiation (which is independent of pressure when the latter is sufficiently high for all the radiation to be absorbed)

can be found, and the absorption-coefficients in the two gases determined. These are given in the following table in cm. units:

	Iron.	Copper.	Zinc.	Arsenic.	Tin.
Air	87·2	51·9	42·7	27·43	3·97
Hydrogen..............	17·05	9·55	7·71	—	0·51

It was deduced on various assumptions (1) that the ratio between the energy absorbed by the silver and that used in producing cathode radiation is constant; (2) that the total cathode ionisations in air and hydrogen are the same; (3) that a linear relation holds between the absorption of the generating *X*-rays in aluminium and that of the generated cathode radiations in air; (4) that the secondary *X*-rays used produced 175 times more ionisation in air than hydrogen (except tin *X*-radiation, for which the ratio is 25). F. S.

French and German Units of Measurement for Radioactive Emanation. A. Jaboin and G. Beaudoin (*J. Pharm. Chim.*, 1910, [vii], 1, 497—499).—The French unit is the quantity of emanation disengaged per minute by 1 mg. of radium bromide in solution, without reference to spontaneous destruction. This unit is independent of the measuring instrument, and remains constant. The German unit is equal to a fall in tension at the electroscope of 1 volt per hour and per litre of radioactive water, and is dependent on the capacity of the measuring instrument. The author has compared the values of the two units by means of the same electroscope, and finds that the French unit is 7000 times as great as the German unit. It is suggested that a common international unit should be adopted.

T. A. H.

The Atomic Weight of the Radium Emanation. André Debierne (*Compt. rend*, 1910, **150**, 1740—1743).—A new method is described for the determination of the atomic weight of the radium emanation based on Bunsen's determination of the density from the velocity of escape of a gas through a small hole in a thin partition. The emanation, mixed with varying amounts of foreign gases, was allowed so to escape from a vessel of 45 c.c. capacity, serving also as a McLeod gauge, at a pressure of about 0·01 mm. of mercury into a much larger vessel maintained vacuous by a Gaede pump kept in continuous operation. The pierced diaphragm consisted of a piece of platinum foil, 0·01 mm. thick, and communication could be made or interrupted at will by a wide-bore tap. The pressure in the guage, with the gas escaping, diminished exponentially with the time over a range from 0·2 to 0·002 mm., and the exponential-coefficient was found to be inversely proportional to the density of the gas for sulphur dioxide, carbon dioxide, oxygen, and argon. For a mixture of oxygen and argon, each gas behaved under the conditions as if alone present at its partial pressure. For the emanation, the amount remaining was determined by means of the penetrating radiation after equilibrium had been attained, and the amount of foreign gas, between the limits of 0·5 and 20 per cent. of emanation, had no effect on the rapidity of escape of the latter. From the exponential-coefficient of escape, the molecular

weight of the radium emanation, as compared with the results for argon and oxygen, was found to be in the neighbourhood of 220. The variations in the separate experiments were not greater than 2 or 3 per cent. This is in remarkable accord with the disintegration theory, from which a molecular weight of 222·5 is to be expected. F. S.

The Quantitative Measurement of the Radium Emanation. WILLIAM DUANE and A. LABORDE (*Compt. rend.*, 1910, 150, 1421—1423; *Le Radium*, 1910, 7, 162—164. Compare Abstr., 1905, ii, 219).—The paper deals with the determination of the constants C and K in the previously-proposed formula: $I_0 = C - K.S/V$, which expresses the initial ionisation, I_0, due to a given quantity of emanation in a cylinder of length about double the diameter, of interior surface, S, and volume, V, C being the ionisation that would be produced were all the radiation absorbed in the air. The ratio K/C had previously been found to be 0·517, so that the above formula may be written: $I_0 = C(1 - 0{\cdot}517.S/V)$. Where I_0 represents the initial current in *E.S.U.* produced by the emanation generated by 1 gram of radium per second, C has the value 5·19. The volumes of the cylinders varied from 10 to 0·44 litres. The maximum current, produced after three hours, is similarly represented by $I_{\text{max.}} = 13{\cdot}15(1 - 0{\cdot}572.S/V)$. The results have been checked by means of standards of radium, for which Mme. Curie found the atomic weight 226·5. F. S.

The Amount of Radium Emanation in the Lower Regions of the Atmosphere and its Variation with the Weather. JOHN SATTERLY (*Phil. Mag.*, 1910, [vi], 20, 1—36).—A long series of successive daily measurements at Cambridge, England, of the amount of radium emanation in the air, by the method of absorbing the emanation in a known volume of air by means of cocoanut charcoal, have been co-ordinated with the prevailing meteorological conditions. The term radium equivalent signifies the amount of radium which would be in equilibrium with the emanation in one cubic metre of air. The average radium equivalent was 105, the lowest 35, and the highest 350 ($\times 10^{-12}$ gram). The average number corresponds with 1·7 emanation molecules per c.c. of air. The amount was found to be lowest during cyclones and highest during anticyclones, except where, from a study of the trajectories of the surface air-currents, the air was known to have travelled over the sea or very rapidly over the land, when it was low. It was high when the air had spent much time over land. The number of ions produced per second per c.c. of air by the emanation averages 2·1 (max. 7·0, min. 0·7). The average emanation content found by Eve at Montreal is 6/11 of the amount found at Cambridge. The lowest number of ions produced per second in a closed vessel is 8 (by Wright in a zinc vessel in the open air on the ground near the Toronto Physical Laboratory, while on the frozen surface of the non-radioactive waters of Lake Ontario the number was 4 for the same vessel). Of these 8, 4 therefore are due to the penetrating radiation from the ground, and, since 1 in Canada (or 2 in Cambridge) is due to the radium emanation, the remaining 3 must be ascribed to the radioactivity of the vessel. In the free air, it is estimated that the

penetrating rays produce 1 instead of 4, and the thorium emanation 2, in addition to the 1, or 2, due to the radium emanation, making a total of 4, or 5, ions per c.c. per second. F. S.

The Solubility of the Radioactive Emanations in Liquids. R. W. BOYLE (*Trans. Roy. Soc. Canada*, 1909, [iii], 3, III, 75—80).—Experiments on the bubbling of thorium emanation in similar manner through different liquids showed that, as for the radium emanation, petroleum oils are the best absorbers, and then follow in order: ethyl alcohol, sulphuric acid, water. Rising temperature diminishes the absorbing power, and so also do dissolved salts, although in relatively small degree. F. S.

The Radioactivity of the Rocks of the Transandine Tunnel. ARNOLD L. FLETCHER (*Phil. Mag.*, 1910, [vi], 20, 36—45).—Nineteen specimens of rock (mostly varieties of tuff, trachyte, and andesite) taken at levels about 1000 feet from the surface in the transandine tunnel, from 2·4 to 4·7 km. from the Argentine end, were examined for radium and thorium content by Joly's methods. For the former, the mean value was $0·79 \times 10^{-12}$ gram of radium per gram (maximum 1·4, minimum 0·3), and for the latter $0·56 \times 10^{-5}$ gram of thorium per gram (maximum 1·1, minimum 0·0), the ratio of the mean thorium to the mean radium ($0·71 \times 10^{7}$) being similar to that found by Joly for certain lavas (Abstr., 1909, ii, 848). Thus these rocks are strikingly low in radioactive matter, which may be due to the alterations most of the rocks had undergone, and the removal of soluble radioactive matter by percolating water. The total heat evolved is estimated at $2·9 \times 10^{-10}$ calorie per hour per gram, in agreement with the fact that no abnormally high degree of temperature was experienced in the tunnel. F. S.

Non-radioactive Minerals Containing Helium. ARNALDO PIUTTI (*Le Radium*, 1910, 7, 146—149).—With different mixtures of pyrolusite and uranium oxide, 1 gram of which was spread over a surface of 4·55 cm.^{2}, the radioactivity could be detected with 0·0001 part of uranium oxide, but not with one-half this proportion. Many minerals of which the radioactivity was too feeble to be detected, for example, castorite, several varieties of tourmaline, and a rose-beryl from Elba, also tourmalines from France, Swaziland, New York, and Madagascar, gave clear indications of the stronger lines of helium when quantities of 1 to 4 grams were heated in a charcoal vacuum. The non-radioactive minerals, however, always contain less helium than the radioactive. In the case of a Madagascar tourmaline, existing in large crystals coloured rose or violet internally with an external fairly sharply defined layer of green colour, the latter possessed a radioactivity and helium-content much greater than the interior portion. For beryls from Elba an inactive rose variety possessed more helium than a green one, which was feebly active. In the beryl from Acworth (New Hampshire) examined by Strutt and found by him not to contain radium, other radioactive substances must be present, for it possesses feeble radioactivity. F. S.

The Radioactivity of the Spring Water of Mülhausen (Alsace). WOLF JOHANNES MÜLLER (*Physikal. Zeitsch.*, 1910, **11**, 545—547).—The spring water of Mülhausen was found to possess a radio-activity of about 8 Mache units by means of the apparatus of Schmidt and Kurz. Such a high activity has so far only been observed for medicinal springs. The activity was proved to be entirely due to dissolved radium emanation, and there is no detectable permanent activity in the water. F. S.

The Radioactivity of Greek Medicinal Springs. TELEMACHOS KOMNENOS [with ANASTAS DAMBERGIS and BASIL AEGINITIS] (*Chem. Zentr.*, 1910, i, 1634; from *Pharm. Post*, 1910, **43**, 189—190).—The radioactivity of the medicinal springs of Aedipsos, Hypati, Cyllene, Loutraki, and Methana is tabulated in electrostatic units. For some (Cyllene) the activity is remarkably small, while for others (Loutraki, Tombasi) it approaches that of the most radioactive springs known. The activity of the springs is supplemented by analytical and temperature details. F. S.

The Rays of Potassium. E. HENRIOT (*Compt. rend.*, 1910, **150**, 1750—1751).—The radioactivity of various potassium salts is nearly proportional to the content of potassium, and the small differences may be ascribed to differences in the absorption in the salts themselves, and to the fact that some of them are deliquescent. No difference of radioactivity was caused by variation of the temperature between 14° and 140°. The rays from the sulphate and chloride possess the same penetrating power. No phenomenon, not atomic in character, gives rise to electrons travelling with velocities as great as in the case of the potassium radiation, which must be regarded as specific to the atom of potassium. F. S.

The Electric Charges Acquired in High Vacua by Insulated Potassium Salts and other Radioactive Substances. J. C. MCLENNAN (*Trans. Roy. Soc. Canada*, 1909, [iii], **3**, III, 81—99).—A considerable surface, in some cases, of the substances examined was exposed in a high vacuum on insulated trays connected to an electrometer. With polonium the substance acquired a positive charge, indicating that more negative than positive electricity was radiated. The same held true, but the effect was much more marked, with an aluminium tube containing radium, the secondary rays excited by the γ-rays in the aluminium causing the action. With uranium nitrate no indication of any charging effect was obtained until the surface was covered with thin aluminium foil to absorb the positively charged α-rays, when a positive charge was acquired. Hence the amounts of positive and negative electricity radiated in this case are similar. With potassium chloride and sulphate, using an apparatus set up with extreme care, the acquisition of a feeble positive charge was proved. The effects were small, but showed that potassium emits an excess of negatively charged particles. It has not yet been determined whether any positively charged particles are emitted. F. S.

Behaviour of Bound Electrons in Solid Substances towards Electromagnetic Radiation. JOHANN KOENIGSBERGER and K. KILCHLING (*Ann. Physik*, 1910, [iv], 32, 843—867).—A theoretical paper in which the observations recorded previously (Abstr., 1909, ii, 367) are examined from the standpoint of the electronic theory. Various methods of calculating the ratio e/m from dispersion and adsorption measurements are indicated. H. M. D.

Electrical and Optical Measurements in the Glow Discharge in Sodium and Potassium Vapour. GEORG GEHLHOFF and KARL ROTTGARDT (*Ber. Deut. physikal. Ges.*, 1910, 12, 492—505).—The electric discharge through potassium and sodium vapours at higher temperatures is accompanied by complete absorption of the residual gases in the discharge tube. The lower limits of temperature at which this occurs are 175° for potassium and 290° for sodium. Potential measurements show that the total and the cathode potential differences fall to a minimum at the temperatures at which absorption commences. With an iron cathode, the normal cathode fall of potential in potassium vapour is 80 volts, in sodium vapour about 115 volts.

The emission spectrum of the anodic glow light shows both the principal and secondary series of lines. In the case of potassium, the negative glow light shows the secondary series at low temperatures; above 230° the fundamental spectrum is seen together with the secondary lines, and above 300° the principal series makes its appearance. In the case of sodium vapour, principal and secondary series are found in the spectrum of the negative glow light at lower temperatures. As the temperature rises, the lines of the secondary series disappear with the exception of that in the green. H. M. D.

Electrochemistry of Proteins. Dissociation of Potassium Caseinogenate in Solutions of Varying Alkalinity. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, 14, 528—568. Compare Abstr., 1908, i, 1027).—The conductivity of potassium hydroxide is at first depressed by the addition of caseinogen, but rises again and attains its original value when the solution is saturated with caseinogen.

The alkalinity of solutions of potassium hydroxide with and without caseinogen was estimated by the hydrogen electrode method. The two solutions were contained in the arms of a U-tube separated by a partition of agar-agar saturated with potassium chloride. The difference in hydroxyl ion concentration, that is, the proportion of unneutralised hydroxide in presence of the caseinogenate, was calculated by Nernst's formula from the potential difference set up. Further, by subtracting the conductivity of uncombined alkali from the total electrolytic conductivity, the conductivity of potassium caseinogenate was obtained.

To promote the dissolution of caseinogen, an excess of alkali was taken, and was afterwards neutralised with hydrogen chloride. The conductivity of potassium caseinogenate is not affected by small quantities of potassium chloride in its solution. Potassium caseinogenate, therefore, does not give the potassium ion, but probably dis-

sociates into complex multivalent ions. The mobility of the potassium ion is about 61×10^{-5} cm. per sec. under unit potential gradient. If the velocity of the caseinogen ion were 15×10^{-5}, the maximum molecular conductivity of potassium caseinogenate would be 73×10^{-3} ohms. at 18°. Conductivities ranging from 80×10^{-3} to 120×10^{-3} were observed. As the caseinogen becomes more concentrated its combining capacity for potassium decreases, but the "molecular" conductivity of the caseinogenate increases. Concentration leads to increased complexity of the caseinogen molecule and increased facility for the formation of complex multivalent ions.

The same hypothesis explains why the sum of the apparent velocities of the ions of ammonium caseinogenate is less than the velocity of the ammonium ion alone. The acidity of caseinogen, according to the gas electrode measurements, tends to become proportional to the concentration of alkali at low alkalinities, but approaches a constant maximum in presence of excess of alkali, 180×10^{-5} gram-molecules of hydroxide combining with 1 gram of caseinogen. On precipitation with ammonium sulphate, some of the alkali is eliminated from the caseinogenate.

The potentiometer determinations show that in those solutions containing no free hydroxyl ions, each gram of casein was combined with 51×10^{-5} gram-molecules of potassium hydroxide at 30°. Previous observations by the titration method have given 50×10^{-5} equivalents as the amount of alkali required to produce neutrality to litmus.

The depression in conductivity of a solution of potassium hydroxide at 30°, $\lambda \times 10^5, = 2680b - 475800b^2/c - 28{\cdot}98c$, where b is the concentration of alkali, and c the percentage of caseinogen. By exterpolation the conductivity of the alkali would be unaffected ($\lambda = 0$) when $b = 0{\cdot}00114c$. This is actually the ratio between b and c in solutions which are saturated with caseinogen. R. J. C.

Absorption of Electrical Waves by Alcohols. P. BEAULARD (*Compt. rend.*, 1910, **151**, 55—57. Compare Abstr., 1906, ii, 3).—The author has determined the apparent specific inductive capacity, ϵ, of glycerol and twelve monohydric alcohols for wave-lengths of 12 and 35 metres, and employed the results to calculate the value of χ in the expression $\epsilon = n^2(1 - \chi^2)$, using Drude's values for n^2, the true specific inductive capacity. With the exception of allyl alcohol all the compounds examined showed anomalous dispersion for electrical waves. W. O. W.

Dielectric Cohesion of Argon. EDMOND BOUTY (*Compt. rend.*, 1910, **150**, 1643—1647. Compare Abstr., 1904, ii, 309).—The critical sparking potential in a given sample of argon at constant pressure is subject to large secular variations, which render the value of the dielectric cohesion somewhat uncertain. If y is the minimum sparking potential, b the cohesion, and p the pressure, $y = a + bp$, where a is a coefficient depending, not only on the gas, but on the nature and condition of the containing surfaces. It is shown that with argon a may be greatly influenced by the presence of mercury vapour from the pressure gauge, and also by preliminary cooling of the argon in liquid air.

By measuring y at three different pressures as quickly as possible, values of a and b were obtained on the assumption that a did not vary during the time taken by the measurements.

A series of determinations made in this way from time to time gave a constant value, 38, to the dielectric cohesion, b, whilst a varied from 539 to 659. With argon recently cooled in liquid air, a is practically zero, but rises in a few days to 800—900.

The value 38 of the cohesion is practically identical with that previously obtained, 39, using argon from another source.

R. J. C.

Photoelectric Effect Exhibited by Zinc in Hexane. GEORGE JAFFÉ (*Physikal. Zeitsch.*, 1910, **11**, 571—575).—Experiments are described which show that zinc, immersed in hexane, has photoelectric properties similar to those exhibited by the metal when surrounded by air. The relative intensities of the photoelectric effect in the two cases depend on the strength of the electric field, on the nature of the incident ultra-violet light, and on the length of time during which the metal has been exposed to the incident rays. In a special case the effect in hexane was found to be about one-thousandth of the corresponding effect in air. H. M. D.

Platinum-Rhodium Thermo-element from 0° to 1755°. ROBERT B. SOSMAN (*Amer. J. Sci.*, 1910, [iv], **30**, 1—15).—In a previous paper (compare this vol., ii, 261) the *E.M.F.* of the platinum-rhodium thermo-element has been referred to the scale of the nitrogen thermometer between 400° and 1550°, and the comparison, and hence the behaviour of the nitrogen thermometer, is now extended to the m. p. of platinum, 1755°, and also from 0° upwards. The above value for the m. p. of platinum has been further confirmed by extrapolation of the curves of thermo-elements containing 1—15% rhodium, and is probably accurate within 5°. The data for the low temperature-interval are the m. p. and b. p. of water, the b. p. of naphthalene, 217·7°, of benzophenone, 305·4°, and the m. p. of cadmium, 320·2°. A simple method of interpolating temperatures with the 10% thermo-element is described.

The variation with temperature of the thermal *E.M.F.* of platinum-rhodium alloys has been determined, and is shown graphically. At all temperatures the *E.M.F.* increases very rapidly with the first additions of rhodium, and at 20% the value has already reached within 80% of the *E.M.F.* of platinum against pure rhodium. The rate of variation of the *E.M.F.* with temperature is also plotted against the atomic composition of the alloy. The data indicate that from 0 to 55 atom per cent. of rhodium solid solutions, but no compounds, are formed. G. S.

The Lead Coulombmeter. I. FRANZ FISCHER and KARL THIELE (*Zeitsch. anorg. Chem.*, 1910, **67**, 302—316).—The object of the investigation is to determine the most suitable lead salts for use as electrolytes in the lead coulombmeter.

Hydrogen borofluoride, purified by adding a small quantity of lead

carbonate to precipitate sulphuric and hydrofluoric acids, filtering, passing hydrogen sulphide, and passing air through the filtrate, dissolves lead carbonate without becoming turbid. The solution of lead borofluoride is neutral to Congo-red, but acid to litmus. Crystals are obtained by cooling to 0°, or by evaporating in a vacuum, but they are highly deliquescent, and cannot be freed from liquid. They leave a basic residue when re-dissolved in water. Alcohol precipitates a hygroscopic, basic salt.

Lead aluminofluoride is prepared by dissolving aluminium hydroxide in hydrofluoric acid, adding a little lead carbonate, filtering, and saturating the filtrate with lead carbonate. The solution attacks glass.

Lead silicofluoride is prepared in a similar manner, and has not been obtained in a crystalline form. Lead titanifluoride and zirconifluoride have similar properties.

Complex acids containing tin are best prepared by dissolving stannous fluoride or stannic sulphide in hydrofluoric acid. The stannous solution only contains a small proportion of complex acid, most of the tin being present as stannous fluoride. Lead stannifluoride resembles the other salts of the same group.

Ceric hydroxide dissolves in hydrofluoric acid, but the complex acid decomposes slowly, depositing cerous fluoride. Lead tetra-acetate and hydrofluoric acid also yield an unstable complex acid, which only dissolves a small quantity of lead carbonate. Vanadium yields a complex acid, which only dissolves small quantities of lead.

Arsenic and antimony trisulphides only form small quantities of complex acids when dissolved in hydrofluoric acid, but arsenic and antimony pentasulphides yield solutions which dissolve lead carbonate, although only a part of the salts is present in the complex form. Bismuth peroxide dissolves in hydrofluoric acid at $-10°$, but the product decomposes when the temperature rises. It was not found possible to compare complex fluorides containing thallium, thorium, or phosphorus.

When the lead salts are electrolysed, lead is deposited quantitatively from the borofluoride and silicofluoride, and probably, under suitable conditions, from the titanifluoride and zirconifluoride; antimony and arsenic are partly deposited with lead, and the deposition from other solutions is not quantitative.

Tin and antimony may be separated by oxidising the solution, passing hydrogen sulphide, and dissolving the precipitate in hydrofluoric acid. Hydrogen sulphide then precipitates only the antimony from the solution. The tin is recovered after decomposing the complex fluoride with sulphuric acid in a platinum basin. Ammonium fluoride may also be used for the extraction of the mixed sulphides, but with less advantage. C. H. D.

The Lead Coulombmeter. II. FRANZ FISCHER, KARL THIELE, and EDWARD B. MAXTED (*Zeitsch. anorg. Chem.*, 1910, **67**, 339—356. Compare preceding abstract).—One copper and two lead coulombmeters are connected together in series. The lead anodes are plates 6×4 cm. in size, and the cathodes are of platinised platinum foil, 6×6 cm. and

0·03 mm. thick, the distance between anode and cathode being 1·5 cm. Copper foil, freshly coated with copper, is used as cathode in the copper cell.

After an experiment, the platinum carrying the deposit of lead is rapidly washed, then lowered into a vessel containing alcohol, and dried in a vertical position in a vacuum desiccator.

For the analysis of the electrolyte, an excess of *N*/10-chromic acid solution is added, the precipitate of lead chromate filtered off, and the excess of chromic acid estimated by means of potassium iodide and sodium thiosulphate. When lead phenol-*p*-sulphonate is used, this method is inapplicable, and the lead is estimated gravimetically. The acidity of the electrolyte is estimated by precipitating the lead with a known excess of sulphuric acid, filtering, and titrating the filtrate with alkali.

Experiments have been made with lead borofluoride, silicofluoride, and phenol-*p*-sulphonate. Too high a proportion of free acid leads to the liberation of hydrogen and the formation of lead sponge, and too low a proportion to crystallisation of the lead. The concentration should increase with the current density, and gentle warming increases the density of the deposit.

A solution of lead borofluoride containing 150 grams of lead and the same weight of free acid per litre gives good results, and may be used for current densities of 0·14—14·0 amperes per sq. dm. A solution of lead silicofluoride of the same, or of lead phenol-*p*-sulphonate of one-half this, concentration also gives good results for ranges of 0·14—11·0 and 0·14—4·9 amperes per sq. dm. respectively. The addition of 0·1—1 gram of gelatin or agar-agar prevents crystallisation, and does not interfere with the accuracy of the determination. C. H. D.

The Theory of the Determination of Transference Numbers by the Method of Moving Boundaries. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1910, 32, 862—869).—In the case of certain solutions, for example, the normal solutions of sodium and potassium chlorides, the transference numbers of the ions have been determined by three methods, namely: (1) the Hittorf method; (2) the method of moving boundaries, and (3) Nernst's method, which gives the "true transference number," and depends on the use of some reference substance in solution which does not wander with the current, and with respect to which rather than to the water the salt content at each electrode is determined. The close agreement obtained by methods (2) and (3) has led Washburn (Abstr., 1908, ii, 1009) and Denison (this vol., ii, 15) to draw the conclusion that the method of moving boundaries gives immediately the true transference numbers. The author shows, however, that this agreement is entirely accidental, and due to the neglect of a correction which must always be made when the method of moving boundaries is employed. This correction is due to volume changes at the electrodes brought about by the disappearance of salt from, or the entrance of salt into, the solution; it is the larger the more concentrated the solution. When this correction is applied, the method of moving boundaries gives,

theoretically and practically, the Hittorf transference numbers, and not the true transference numbers.

The theory of a suggested method for obtaining true transference numbers from moving boundary experiments by the aid of a non-electrolyte which does not migrate with the current is given, but the method still remains to be worked out practically. T. S. P.

Electrolytic Conductivity of Non-aqueous Solutions at Low Temperatures. PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1910, **73**, 257—268. Compare Abstr., 1904, ii, 227; 1906, ii, 149, 335; 1907, ii, 231, 734).—Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, 338) has shown that the temperature-coefficient of the conductivity a of aqueous solutions approximates to the temperature-coefficient of the fluidity of water, and the author (*loc. cit.*) has found that the same relationship is approximately valid for organic solvents. In the equation $K_t = K_0(1 + at)$, K_t, the specific conductivity at the temperature t, must become zero at the temperature $t_x = -1/a$, provided that the relationship in question holds for low temperatures.

To test this point, the conductivity of tetraethylammonium iodide or the corresponding propyl compound has been determined in twelve organic solvents through a wide range of temperature, in some cases from $-100°$ upwards. The results show that in no case does the temperature-conductivity curve intersect the temperature axis at an acute angle, as required by the above considerations, but approaches it asymptotically, so that the calculated values of t_x for the different solvents have no definite physical meaning. In the course of the experiments, the freezing points of the following substances have been re-determined: ethylene glycol, $-11{\cdot}2°$; furfuraldehyde, $-36{\cdot}5°$; anisaldehyde, $-2{\cdot}1°$; methyl cyanoacetate, $-22{\cdot}5°$; phenylacetonitrile, $-26{\cdot}5°$; methyl thiocyanate, $-51°$, and nitromethane, $-26{\cdot}5°$.

G. S.

Formamide as a Solvent for Inorganic Salts and the Electrolysis of Such Solutions. HERMANN ROHLER (*Zeitsch. Elektrochem.*, 1910, **16**, 419—436).—The specific volume of pure formamide between $-7°$ and $+25°$ is given very exactly by $V = 0{\cdot}8674(1 + 0{\cdot}000644t)$. There is no maximum between these limits. The purest material obtained had m. p. $1{\cdot}58°$, and specific conductivity, $18{\cdot}9 \times 10^{-5}$.

Anhydrous copper sulphate dissolves in formamide, yielding a dark blue solution, which soon deposits a light blue, crystalline cupric formamide of the composition $(H{\cdot}CO{\cdot}NH)_2Cu + 2H{\cdot}CO{\cdot}NH_2$. By prolonged heating at 95°, two molecules of formamide are driven off, leaving copper formamide, $(H{\cdot}CO{\cdot}NH)_2Cu$. The sulphuric acid produced remains dissolved (partly in combination with formamide), and its accumulation limits the reaction. The acid solution, with 0·8% of copper, was electrolysed, using a copper anode and a rotating cathode. The quantity of copper deposited was much less, and that dissolved much greater, than the theoretical amount. It was found that copper reduces the cupric salt to cuprous salt, and also that formamide alone dissolves copper in presence of oxygen. By shaking

the cupric solution with copper until reduction was complete, and then carrying out the electrolysis in an atmosphere of hydrogen, equal quantities of copper were dissolved and deposited. At 25°, only 29% of the cupric salt is reduced by metallic copper, and the quantity of copper deposited when the solution is electrolysed is about 4/3 of that deposited simultaneously in a copper voltameter.

A saturated solution of cuprous chloride in formamide is colourless, and contains 1·3% of copper; when electrolysed in an atmosphere of hydrogen, the copper dissolves, and is deposited quantitatively in the univalent form. With both the sulphate and chloride solutions the deposits are powdery at first, but improve with continued use of the solution. Lustrous, adherent deposits are obtained with about 0·2 to 0·25 ampere per 100 sq. cms.

Salts of mercury and silver are reduced to metal by formamide; this is also the case with the copper solutions when they are warmed.

Cupric chloride and formamide react in the same way as the sulphate. The hydrochloric acid formed combines with formamide to a colourless, crystalline substance, $H\cdot CO\cdot NH_2,3HCl$. The solutions of this substance in formamide conduct electricity well, and dissolve zinc with evolution of hydrogen.

The chlorides of nickel and cobalt react readily with formamide, yielding crystalline compounds: $Ni(CH_2ON)_2,2CH_3ON$ and $Co(CH_2ON)_2,2CH_3ON$ respectively. Like the copper compound, these decompose when heated, leaving a residue of pure metal.

Lead nitrate gives the compound $Pb(CH_2ON)_2$, but lead chloride takes up a molecule of formamide without decomposition, yielding the substance $PbCl_2,CH_3ON$. Lead formamide decomposes at 200°, leaving metallic lead.

Stannous chloride is very freely soluble in formamide, and reacts with it, but the compound could not be isolated.

Zinc chloride dissolves readily, and the strong solutions deposit zinc formamide, $Zn(CH_2ON)_2,2CH_3ON$; when heated at 100°, this decomposes, losing formamide and water and leaving zinc cyanide.

The metallic formamides are all sparingly soluble in formamide; the solubilities lie between $0·2N$ and $0·005N$ at 25°. The conductivity of the solutions is small.

Solutions of lead chloride (4% of lead), lead nitrate (31·5% of lead), zinc chloride (8·2% of zinc), zinc oxide (0·8% of zinc), and of stannous chloride (14·3% of tin) were electrolysed in the same way as the copper solutions. In each case, compact, adherent deposits were obtained under almost the same conditions described for copper, and, except that no reduction occurs, the results were very similar.

No metallic deposit was obtained when solutions of nickel, cobalt, iron, aluminium, and magnesium salts were electrolysed. T. E.

Electrolysis of Glass. ADOLF HEYDWEILLER and F. KOPFERMANN (*Ann. Physik*, 1910, [iv], **32**, 739—748).—Experiments are described which show that sodium, potassium, barium, strontium, tin, lead, copper, iron, cobalt, and silver are capable of passing through glass at temperatures of 250—450° under the influence of an electric field.

Negative results were obtained with gold, platinum, and uranium. The glass diaphragm, in the form of a tube, the thickness of which varied from one to two millimetres, was immersed in a molten salt of the metal under investigation, and this served as the anode liquid. The cathode liquid, consisting usually of a mixture of sodium and potassium nitrates, was placed in the tube itself. Similar results were obtained with an easily fusible sodium glass and a much less readily fusible potassium glass.

In many cases the entry of the foreign metal ions into the glass is accompanied by the appearance of pronounced colour effects. These are attributed to the colloidal condition of the metals, and this view is consistent with the appearance of the glass under the ultramicroscope. In general, the conductivity of the glass varies as the electrolysis proceeds, and this is supposed to be due to differences in the mobilities of the various ions.

Similar diffusion phenomena are observed without an electric current, but the process in these circumstances is comparatively slow. H. M. D.

Magnetisation of Certain Alloys as a Function of the Composition and the Temperature. Kōtarō Honda (*Ann. Physik*, 1910, [iv], 32, 1003—1026).—The dependence of the magnetic properties of binary alloys on the composition and on the temperature has been examined. Data were obtained for the following pairs of metals: nickel–chromium, cobalt–chromium, iron–vanadium, nickel–tin, nickel–aluminium, manganese–antimony, and manganese–tin. From a comparison of the magnetic data with observations relating to the structure of the alloys, it is found that the ferro-magnetic properties are determined by particular crystalline constituents of the alloys. This is also true in the case of the remanent magnetism. H. M. D.

Thermo-magnetic Properties of the Elements. Kōtarō Honda (*Ann. Physik*, 1910, [iv], 32, 1027—1063).—The magnetic susceptibility of a large number of elements has been determined at the ordinary and at higher temperatures. A comparison of the data for the ordinary temperature shows that the magnetic susceptibility varies with the atomic weight in a periodic manner. Elements belonging to the same group occupy in many cases corresponding positions on the periodic curve. In respect of the influence of temperature on the magnetic susceptibility, the various elements are tabulated according to whether the susceptibility increases, decreases, or remains practically constant as the temperature rises. H. M. D.

A Graphic Method for the Correction of Gas Volumes. Robert Crosbie Farmer (*Analyst*, 1910, 35, 308—309).—A convenient device for the reduction of gas volumes to normal temperature and pressure, the various scales being so arranged that, by means of a rule placed at the points corresponding with the observed temperature and pressure, the corrected volume of 1 c.c. of gas at normal temperature and pressure can be read off. For nitrogen estimations a scale has been added by which the logarithm of the weight of 1 c.c. of nitrogen can be read. L. de K.

Gaseous Explosions. SIR WILLIAM H. PREECE, DUGALD CLERK, BERTRAM HOPKINSON, WILLIAM A. BONE, BURSTALL, HUGH L. CALLENDAR, ERNEST G. COKER, W. E. DALBY, HAROLD B. DIXON, RICHARD T. GLAZEBROOK, H. S. HELE-SHAW, J. E. PETAVEL, ARTHUR SMITHELLS, W. WATSON, JOHN A. HARKER, H. C. L. HOLDEN, and H. R. SANKEY (*Brit. Assoc. Report*, 1909, 247—270).—This report deals with the measurement of the specific heat of gases at high temperatures, radiation in gaseous explosions, the measurement of temperature, and Deville's experiments on the dissociation of gases.

E. H.

Thermodynamics of *iso*Pentane. GÜNTHER VOGEL (*Zeitsch. physikal. Chem.*, 1910, **73**, 429—480).—As a preliminary to the discussion of the characteristic equation for *iso*pentane, the experimental data of Young for this substance have been supplemented by direct determinations of certain thermal constants. The heat of vaporisation is $6397 \pm 19{\cdot}88$ cal. per mol.; the specific heat of the vapour at constant pressure is 0·4593 at 58° and 0·4881 at 100·75°, and the specific heat of liquid *iso*pentane determined by comparison with benzene is $0{\cdot}5266 \pm 0{\cdot}00106$ at 8°.

On the basis of the characteristic equation of Reinganum (*Diss.*, Gottingen, 1899), which is a modified form of van der Waals' equation, the equation $a = \left(T\frac{\delta p}{\delta T} - p\right)v^2 = \left[\alpha + \beta + \gamma\frac{\rho_0 - \rho}{1 + c\rho^9}\right]e^{-T^4/k^1}$, where $\rho = 1/v$, and α, β, γ, c, k^1 are constants, is deduced, and is shown to represent satisfactorily the thermal behaviour of *iso*pentane. From this expression by integration the somewhat complicated characteristic equation for *iso*pentane is obtained.

Finally, the above expression $a = [T(\delta p/\delta T) - p]v^2$ is shown to hold also for ethylene, ethyl ether, and carbon dioxide, and it is probable that the behaviour of these substances could also be represented by characteristic equations similar to that deduced for *iso*pentane.

G. S.

Method for Determining Boiling Points under Constant Conditions. ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, **30**, 432—435).—The apparatus consists of a small bulb with a bent capillary not less than 1 mm. in diameter. The bulb is charged with 0·03—0·1 gram of the substance of which the boiling point is to be determined, and attached to a thermometer suspended in a beaker containing the heating liquid, so that the opening of the capillary points downwards. When the temperature of the bath has remained at the boiling point of the substance in the bulb for a few moments, dissolved and occluded gases and moisture have all been expelled, and a rapid stream of pure vapour issues. With falling temperature and vigorous stirring, the point at which the bubbles suddenly cease can be read accurately; this is the boiling point (compare Abstr., 1909, ii, 20), When the substance is soluble in the bath-liquid, the point at which boiling ceases cannot be ascertained sharply. The bath-liquid is then allowed to recede into the

capillary to a fixed point 5—10 mm. from the opening; the temperature at which this point is reached is the boiling point.

Besides the ordinary correction for barometric pressure, a correction must be made for the head of liquid above the opening of the capillary or above the mark to which the bath-liquid ascends. This depth is measured to within 2 mm., and the density of the bath-liquid may be obtained from the following formulæ: Sulphuric acid (92·75%); $D = 1{\cdot}818 - 0{\cdot}000906\ (t - 30°)$. Melted paraffin (m. p. 53°); $D = 0{\cdot}778 - 0{\cdot}000612\ (t - 60°)$. Mixture of sodium and potassium nitrates (45·5 : 54·5 parts); $D = 1{\cdot}968 - 0{\cdot}00075\ (t - 230°)$.

The method is accurate, and may be applied to non-fusing solids, such as calomel and ammonium carbonate. T. S. P.

A Common Thermometric Error in the Determination of Boiling Points under Reduced Pressure. ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, **30**, 436).—When the bulb of a thermometer is enclosed in an evacuated vessel, the dilatation of the bulb introduces a considerable error into the temperature readings. In the case of some thermometers which were tested, a diminution in pressure from 748 to 20 mm. caused an error of 0·10—0·17°. This source of error has hitherto not been taken into account in measuring boiling points under diminished pressure.

T. S. P.

Simple Dynamic Method for Determining Vapour Pressures. ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, **30**, 437—438).—The bulb apparatus described in a previous abstract is used. The lower part of the thermometer is enclosed in a test-tube containing a portion of the bath-liquid. The interior of the test-tube communicates, through a right-angled tube inserted in the cork, with a pump and with the atmosphere. The bath is brought to constancy at the required temperature with the pressure in the apparatus above the vapour pressure of the substance. The pressure is next lowered gradually until a continuous stream of bubbles issues from the capillary. Then the pressure is allowed to rise until the stream just ceases, which gives the vapour pressure at the temperature of the bath. T. S. P.

Vapour Pressure of Water and Aqueous Solutions of Sodium Chloride, Potassium Chloride, and Sucrose. FRANCIS C. KRAUSKOPF (*J. Physical Chem.*, 1910, **14**, 489—508).—The water contained in a known volume of air saturated at the vapour pressure of each solution was estimated by direct weighing in absorption tubes. From 2 to 28 litres of air were drawn over the solution in about one hour, the volume being so chosen as to give about 1 gram of water in each case. The method and apparatus used were described by Lincoln and Klein (Abstr., 1907, ii, 435), with the difference that heavy gas-engine oil with practically no vapour pressure was used in the aspirator instead of water.

The vapour pressures of water at various temperatures are as follows: 25°, 23·71 mm.; 30°, 31·84 mm.; 35°, 41·91 mm.; 40°,

55·18 mm.; 50°, 92·16 mm.; 60°, 149·26 mm.; 70°, 233·99 mm.; 80°, 355·08 mm. These values are in good agreement with previous observations.

The vapour pressures of sodium chloride and potassium chloride solutions at 40° and 60° show an apparent increase in molecular weight as the solutions become more dilute. This agrees with Kahlenberg's freezing-point and boiling-point determinations, and is opposed to the dissociation theory.

The molecular weight of sucrose appears to decrease with increase in the dilution. R. J. C.

Vaporisation. V. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1910, **73**, 343—382. Compare Abstr., 1908, ii, 663, 810; 1909, ii, 21; this vol., ii, 583).—It is suggested that the deviations from van der Waals' equation are connected with the simultaneous existence of liquid and vapour, and that the equation is strictly valid for a single phase (liquid or vapour). A number of relationships are deduced for "ideal" conditions, that is, when only one phase is present.

For ideal liquids the ideal density is proportional to the temperature. At the absolute zero it is four times the critical density, and is zero at $T''_k = 2T_k$. The temperature T''_k is therefore called the absolute critical point.

$T'_k = 3/2T_k$ is the ideal critical point; at this temperature the ideal density of the liquid is equal to the critical density, and, further, $\pi'_k = 3p'_k$, $v'_k = 3b'_k$, and $v_l/v_k = 8/3$, where the symbols have the usual significance and ideal conditions are indicated by the $'$ sign.

The surface-tension of the ideal liquid is represented by the formula $\pi'_k/\pi_k = a(D_l/D_k)^2 = 4$, and is diminished in the presence of vapour (owing to the capillary attraction of the vapour molecules) to $\pi_k/\pi_v = a(4-1) = 3a$. As the internal pressure is thus reduced, the liquid expands.

If the vapour density is represented by d, the ideal liquid density by D', the relationships hold: $\pi_d = ad^2$, $\pi_l = aD_1^2$, and $\pi_l - \pi_d = a(D_1^2 - d^2)$. When allowance is made for the diminution of the internal pressure, π, of the liquid, the final value of the latter is $a(D-d)^2$. Further, for the ideal liquid the following relationships hold: $D^1/D_k = 4 - 2\theta$; $v'/v_k = 1/(4-2\theta)$, and $\pi/\pi_k = (4-2\theta)^2$ (for meaning of symbols see *loc. cit.*). The above considerations also afford a simple explanation of the law of Cailletet and Mathias, as the density of the ideal liquid in the presence of its vapour is diminished by the density of the vapour.

For further deductions and illustrations the original paper should be consulted. In particular, the relationship $p_k v_k/T_k = \text{const.}$ is deduced, and it is shown from the data for over forty liquids that the deviations from the mean value are extremely small. G. S.

Crystallisation Temperatures of Binary Mixtures. ÉMILE BAUD and L. GAY (*Compt. rend.*, 1910, **150**, 1687—1690. Compare this vol., ii, 268).—A liquid A solidifies at T, where the vapour-tensions of its liquid phase (l) and solid phase (s) become equal. If a second liquid B is added to A, s remains unchanged, but l becomes a partial pressure. Partial pressure is proportional to concentration if the liquids do not interact (compare Dolezalek, Abstr., 1909, ii, 22).

Clapeyron's equation gives for the pure liquid A, $d \log l/dT = EL/RT^2$ and $d \log s/dT = ES/RT^2$, where L and S are the latent heats of vaporisation of pure liquid and pure solid A. Hence $d \log \frac{s}{l}/dT = E(S-L)/RT^2 = EQ/RT^2$, where Q is the latent heat of fusion of A. If now it be assumed that Q is independent of temperature, $\Delta t = -K \log x . T_2$, where x is the concentration of the component A in the mixture depositing pure A at an absolute temperature T_2. The depression of the freezing point is proportional to the logarithm of the molecular concentration of the solvent, and to the absolute freezing point. In very dilute solutions this expression is identical with Raoult's law.

The authors have verified this equation for mixtures of ethylene dibromide with benzene, toluene, and ether, and of ethylene dichloride with benzene. It is claimed that the assumption that $(S-L)$ is independent of temperature is justified by the concordance of the results and the equation. This is also to be taken as evidence that the above liquids are non-associated and do not combine. R. J. C.

Heat of Solidification of Alloys of Lead and Tin. DOMENICO MAZZOTTO (*Nuovo Cim.*, 1910, [v], **19**, i, 215—232. Compare Guertler, this vol., ii, 126).—The author has repeated his experiments made in 1886 on the heats of solidification of tin and of tin-lead alloys, the method adopted being a comparison of the time of cooling of a crucible containing the tin or alloy with that of a crucible containing an equal volume of mercury. The method of calculation does not involve any hypothesis as to the constitution of the alloy, so that Guertler's objection is disposed of. Two sets of experiments have been made, one with the surrounding medium at 15°, and the other with the medium at 100°; the results obtained in the two series agree as well as can be expected. In confirmation of his former results, the author finds that there is a well-marked decrease in the heat of solidification in passing from tin to its alloys with lead, the diminution being nearly proportional to the concentration of lead in the alloy, and he can obtain no indication of the increase which can be deduced from Spring's experiments (Guertler, *loc. cit.*). In the author's opinion the cause of the discrepancy lies in the indirect nature of the calculation by means of which the heats of fusion are obtained from Spring's results, the method being such as to magnify any experimental errors. It is pointed out that the results of Guertler are not independent of those of Spring, but are obtained merely by another mode of calculation.

R. V. S.

Friction in the Bomb Calorimeter. H. A. ROESLER (*Amer. Chem. J.*, 1910, **44**, 80—84).—The heating effect due to the friction of the stirrer in the bomb calorimeter is calculated from the equation: $F = S_1 - \left(\frac{S_1 - S_2}{t_1 - t_2}\right)t_1$, where F is the rate of rise of temperature due to friction, and S_1 and S_2 are the rates of rise of temperature due to radiation plus friction at the temperatures t_1 and t_2. The value of F is most accurately determined when one value of t is nearly zero and the other several degrees above or below. An alternating current

induction fan motor is the best motive power, since it produces the uniform stirring which experience shows to be necessary to give a constant value of *F*. C. S.

Thermochemical Studies. III. Diazo- and Azo-compounds. W. SVENTOSLAVSKY (*Ber.*, 1910, **43**, 1767—1773. Compare this vol., ii, 588).—Thermochemical data are given for the diazotisation of *p*-nitroaniline in aqueous solution, +18·89 Cal., and in acetic acid solution, +18·42 Cal. The heat of solution of the diazonium chloride,

$$NO_2\cdot C_6H_4\cdot N_2Cl,$$

in water is −3·0 Cal. The heat of isomerisation of the diazo-compound into the *iso*diazo-compound in presence of sodium hydroxide is +13·22 Cal., that is, $NO_2\cdot C_6H_4\cdot N_2Cl + H_2O = NO_2\cdot C_6H_4\cdot N_2\cdot OH + HCl - 0{\cdot}48$ Cal. The heat of solution of *p*-nitroaniline in acetic acid is −4·47 Cal., that of the coupling with *β*-naphthol, +26·21 Cal., making a total of 40·16 Cal. for the heat of formation of the azo-dye. This value differs largely from that found for other azo-dyes.

E. F. A.

The Heat of Hydration and Vapour Pressure of the Hydrates of Thorium Sulphate. IWAN KOPPEL (*Zeitsch. anorg. Chem.*, 1910, **67**, 293—301).—The direct measurement of the vapour-pressure of the octa- and tetra-hydrates of thorium sulphate is impracticable, on account of the slowness with which equilibrium is attained. The heat of transformation of one hydrate into the other is also not directly measurable for the same reason, but it may be determined by measuring the difference between the heats of solution. As the solubility in water is very small, it is better to measure the heat of solution in solutions of alkali oxalates or carbonates, the complexity of the reaction being unimportant, as only the difference is required.

A glass calorimeter holding 650 c.c. is used, enclosed in a silvered vacuum vessel, the solvent being 600 c.c. of a 13·32% solution of potassium carbonate. The hydrate is enclosed in a thin glass bulb, which is broken after the temperature has become constant. The heats of solution thus obtained for the octa- and tetra-hydrates respectively are 14944 cal. and 28467 cal., giving the value 13523 cal. for the reaction: $Th(SO_4)_2,4H_2O + 4H_2O = Th(SO_4)_2,8H_2O$. The application of Raoult's formula gives 14424 cal., the vapour-pressures used being calculated from those of the acids with which these hydrates are in equilibrium at the transformation point (compare this vol., ii, 717). Small errors in the vapour pressure, however, give rise to large errors in the heat of transformation.

Using Roozeboom's data for the solubility of the hydrates of thorium sulphate, values for the heat of hydration approximately agreeing with that given above are obtained. C. H. D.

Cause of Disagreement among the Various Methods of Calculating the Deviations from Avogadro's Law. PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, **8**, 222—227).—The recent work of Gray and Burt (Trans., 1909, **95**, 1633) and of Scheuer (Abstr., 1909, ii, 991) gave very concordant values for the density of hydrogen chloride. The atomic weight of chlorine calculated from them varies considerably

according as the corrections of van der Waals' equation are obtained from the compressibility or the critical constants of hydrogen chloride. Comparison with the chemical determinations of the atomic weight of chlorine confirms the figure obtained by use of compressibility data, and suggests that the correction $(1+a)(1-b)$ from the critical data is too great. This should be the case if hydrogen chloride is associated at its critical point. The same considerations applied to the work of Ter Gazarian (Abstr., 1909, ii, 568) indicate that hydrogen phosphide is associated at its critical point.

According to McIntosh and Steele, liquid hydrogen chloride has the association factor 1·5, and liquid phosphine 1·4, whereas hydrogen bromide, iodide, sulphide, and other permanent gases are not associated. This is held to confirm the author's view. R. J. C.

Condensation of Water by Electrolytes. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1910, **14**, 569—575).—The "hydration values" arrived at in a previous paper (this vol., ii, 188) have been found to be generally miscalculated, and also partly founded on incorrect densities. The authors here publish the same tables recalculated, but remark that if the solutes are actually hydrated as their figures indicate, it seems altogether improbable that the density of the dissolved solute is the same as for the solid state; consequently the calculations are meaningless. R. J. C.

Adsorption of Certain Dyes. LÉO VIGNON (*Compt. rend.*, 1910, **151**, 72—75. Compare this vol., ii, 272, 273).—Solutions of various dyes were passed through asbestos and sand, and the amount of adsorption approximately determined. Adsorption was found to occur with equal readiness whether the substance existed in true or colloidal solutions. W. O. W.

Importance of Adsorption for the Precipitation of Suspension Colloids. HERBERT FREUNDLICH (*Zeitsch. physikal. Chem.*, 1910, **73**, 385—423).—The adsorption of the cations of the metallic salts, ammonium chloride, ammonium sulphate, uranyl nitrate, aluminium sulphate, cerium nitrate, and of the following salts of organic bases, aniline hydrochloride, *p*-chloroaniline hydrochloride, morphine hydrochloride, strychnine nitrate, and new-magenta by arsenious sulphide has been determined. As the degree of adsorption is comparatively small and the sulphide could not be obtained absolutely pure, no high degree of accuracy is claimed for the results. The relative activities of the same salts in bringing about the separation of arsenious sulphide from colloidal solution have also been measured.

As far as the organic cations are concerned, those which are most strongly adsorbed are also most active in coagulating arsenious sulphide solutions. On the other hand, the metallic salts investigated, when referred to equimolar concentrations, are adsorbed to about the same extent, and the nature of the anion has very little influence. By means of experiments with uranyl nitrate, cerium nitrate, and the hydrochlorides of aniline and morphine, the general rule has been confirmed that in the coagulation of arsenious sulphide equivalent (not equimolar) amounts of the cations are adsorbed. The coagulation

results with strychnine nitrate proved to be somewhat irregular. Experiments on the coagulation of solutions of colloidal gold confirm the results of previous observers.

The above results are regarded as supporting the adsorption theory of the coagulation of colloidal solutions by electrolytes. The fact that cations of different valency are adsorbed in equimolar proportions is in harmony with the experimental fact that their coagulating powers (which correspond in the first instance with equivalent amounts) are very different. Instead of comparing the relative quantities of different substances required to bring about coagulation, it is preferable for purposes of calculation to subtract from these amounts the quantities adsorbed. G. S.

The Use of Chitin in Dialysis. CARL L. ALSBERG (*Proc. Amer. Soc. Biol. Chem.*, 1909 ; *J. Biol. Chem.*, 1910, **7**, xii).—Excellent dialysers may be made from the lobster's claw, freed from protein, calcareous salts, and acid. It has great strength. Large sheets of chitin can be obtained from the carapace of the horse-shoe crab. There is some evidence that chitin exerts a selective action, but this is still under investigation. W. D. H.

Osmotic Phenomena. WENDELL G. WILCOX (*J. Physical Chem.*, 1910, **14**, 576—595).—The author has measured the osmotic pressures, relative to rubber membranes, of dilute pyridine solutions of sucrose, silver nitrate, and lithium chloride. If osmosis is, as Kahlenberg suggested, a distribution phenemenon in which the solution and the membrane compete for the solvent, it should be possible to make a solution of small but finite dilution, such that the membrane would not give up solvent to it and no osmotic pressure would be developed.

The pyridine used was purified from picolines and water by oxidation with permanganate, followed by repeated distillation over barium oxide. A pyridine boiling constantly at 114·3°/738 mm. was obtained. One % of water lowers the b. p. by 3·5°, and smaller quantities in proportion.

The osmotic cell was an inverted thistle funnel with rubber membrane stretched across. No stirring of the solution was possible, but precautions were taken to exclude moisture, as an experiment usually lasted fifteen days or more. A correction was applied for the solvent which passed in and the solute which passed out through the membrane. The osmotic pressure usually attained a maximum and then dropped again. The maximum in no case attained to 5%, and on the average was only 2·7% of that calculated on the gas laws.

Copper oleate, copper chloride, urethane, carbamide, mercuric chloride, and potassium iodide were found to pass through rubber membranes. R. J. C.

Osmotic Pressure of Colloids. II. Osmotic Pressure of Solutions of Certain Colouring Matters. WILHELM BILTZ and ARVED VON VEGESACK [and, in part, HANS STEINER] (*Zeitsch. physikal. Chem.*, 1910, **73**, 481—512. Compare this vol., ii, 22).—The osmometer already described has been simplified in some respects, and stirring is now found to be unnecessary. Measurements have been made with

Congo-red, night-blue, and benzopurpurin, and the results differ considerably from those previously obtained (*loc. cit.*).

The Congo-red was carefully freed from salts by prolonged dialysis. The osmotic pressure was first measured against a solution of approximately the same electrical conductivity (obtained by concentration of the solution which had passed through the dialyser). The mean molecular weight calculated from these observations was 2333, about three times the normal value, 696, but when measured against pure water in the outer vessel the mean value is about 602, rather less than the normal value, in full agreement with the results of Bayliss (compare Abstr., 1909, ii, 648) obtained in the same way. In no case is a very small molecular weight obtained, corresponding with the fact that Congo-red is considerably ionised, and it is therefore suggested that when only one of the ions is retained by a membrane, the action is due to that ion alone, and when each molecule gives rise to one non-dialysable ion the effect is the same as that of a solution containing only non-ionised molecules. From a consideration of the equilibrium between the ions of the Congo-red and those of the sodium sulphate in the outside solution, the conclusion is drawn that if the solute is not polymerised, the apparent molecular weight should be three times the normal value (that is, 2088), hence the solute is only slightly polymerised, in the ratio 2333 : 2088.

The molecular weight of night-blue is also apparently three times as great when the osmotic pressure is measured against a salt solution of the same conductivity as when it is measured against pure water, but the results in this case are somewhat complicated by hydrolysis.

The molecular weight of commercial Congo-red, which contains about 26% of salts, chiefly sodium sulphate, is about 380, so that the association factor is 7380/2088 = 3·5, and commercial benzopurpurin is still more highly associated. The conclusion that these dyes are more highly associated in the presence of salts is fully confirmed by ultramicroscopic observations.

It is shown by osmotic pressure, ultramicroscopic and viscosity measurements that the degree of polymerisation of night-blue and of benzopurpurin in the presence of electrolytes increases considerably on keeping. Moreover, polymerisation is considerably greater in concentrated than in dilute solutions.

The association factors of night-blue solutions have been determined by osmotic pressure measurements at different temperatures with the following results: 6·7 at 0°, 3·05 at 25°, 2·1 at 50°, and 1·9 at 70°.

G. S.

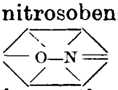
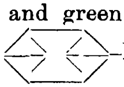
Relative Velocities of Diffusion in Aqueous Solution of Rubidium and Cæsium Chlorides. G. R. Mines (*Proc. Camb. Phil. Soc.*, 1910, **15**, 381—386).—A method of determining the relative rates of diffusion of electrolytes is described, in which an aqueous solution of the electrolyte is placed in contact with a solidified 4% solution of gelatin and the rate of diffusion measured by the electrical conductivity at a fixed distance below the surface of the jelly. For dilute solutions the measured conductivities are very nearly proportional to the concentrations, and when the concentration, determined in this manner, is plotted against the time, curves are

obtained which are convex to the base line at the commencement, and slightly concave towards the end of the experiment. Between these limiting regions the concentration increases at a constant rate, the magnitude of which is regarded as a measure of the velocity of diffusion. For 0·1*N*-solutions of lithium, sodium, potassium, rubidium, and cæsium chlorides, the relative rates of diffusion were found to be 0·684, 0·830, 1·000, 1·023, and 1·055. These numbers increase as the atomic weight and the velocity of the cation increases.

H. M. D.

[Relative Velocities of Diffusion.] A. V. Hill (*Proc. Camb. Phil. Soc.*, 1910, **15**, 387—389).—A mathematical examination of the experimental method described in the preceding paper. It is shown that directly comparable results can be obtained if the depth of the layer of jelly is the same in different experiments. When this condition is satisfied, the intervals of time required to obtain equimolar concentrations are inversely proportional to the diffusion constants of the electrolytes under investigation.

H. M. D.

Molecular Mechanical Theory of Anisotropic Liquids or So-called Liquid Crystals. Th. Rotarski (*J. pr. Chem.*, 1910, [ii], **82**, 23—37).—After reviewing briefly the characteristic properties of liquid crystals and Quincke and Tammann's theories of their formation, the author develops his own views on the subject. He has already shown (Abstr., 1908, i, 374) that some azoxy-compounds form isotropic, others anisotropic, liquids when fused; the latter resemble nitroso-compounds in several respects, and the author is of opinion that there is a close relation between the formation of liquid crystals and the behaviour of nitroso-compounds during fusion. He explains both by assuming the postulate: the attraction of the constituents of a molecule towards its centre increases with lowering, and decreases with rise, of temperature; thus colourless, crystalline nitrosobenzene and green liquid nitrosobenzene are represented by  and —N=O respectively, the group =N—O— changing to the chromophore —N=O. This explanation is also applicable to the behaviour of *p*-nitrosophenol, aliphatic ψ-nitroles, and nitrogen peroxide when heated.

The application of the theory to liquid crystals is as follows. In the solid state the constituents of the molecule are attracted to its centre. When the substance is completely fused to a clear isotropic liquid, the constituents have moved right away from the centre. The intermediate positions, where the constituents have only partly moved from the centre, correspond with the liquid crystalline condition. The three cases may be represented diagrammatically thus:

A–B–C–B–A	Isotropic liquid.
B–C–B | | A A	Anisotropic liquid.
B–C–B ╲AA╱	Crystalline solid.

Substances which form liquid crystals have large molecular weights, and the size of the constituents is favourable to slowness of withdrawal from the centre.

The attraction towards the centre of the molecule, induced by cooling, must depend, not only on the size of the molecule, but also on the magnitude of the attracted groups, because diethylbenzidine forms an anisotropic liquid, whilst dimethylbenzidine is isotropic when fused.

The polymorphism of some anisotropic liquids is sufficiently explained by the preceding and the following diagrams:

$$\left.\begin{array}{c}\begin{array}{ccccccc}A&-&B&-&C&-&B\\&&&&&&|\\&&&&&&A\end{array}\\[1em]\begin{array}{ccccc}B&-&C&-&B\\|&&&&|\\A&&&&A\end{array}\end{array}\right\}\text{ Anisotropic liquids.}$$

C. S.

Transformation of Amorphous into Crystalline Substances. CORNELIO DOELTER (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 29—34).—In reference to Weimarn's view (Abstr., 1909, ii, 132, 134, 221, 306, and 666) that all solid substances are crystalline and that there is no special amorphous form of matter, the author gives a summary of earlier observations bearing on the subject, and discusses the question from the mineralogical standpoint. Although the evidence appears to be in favour of Weimarn's theory, the author considers that the question of the relationship between the apparently amorphous and the crystalline conditions is not yet settled. H. M. D.

Crystalline Solid Solutions as Disperse Systems of Different Degrees of Dispersity. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 35—37).—A quotation from a paper by Frankenheim (*Ann. Physik*, 1860, **111**, 1) is given, in which the peculiarities of the structure of mixed crystals are described. From a consideration of these, the author is led to the conclusion that crystalline solid solutions represent disperse systems which can be divided into two groups: (1) disperse systems of lamellar structure; (2) disperse systems of granular structure. The slow rate of diffusion, which characterises the solid state, is favourable to the formation of highly disperse systems. H. M. D.

Colloido-chemical Theory of the Constitution of Water. HEINRICH SCHADE (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 26—29).—On the assumption that water consists partly of polymerised colloidal molecules which undergo dissociation with the formation of simple water molecules, an attempt is made to explain the abnormal properties of water. Reference is made to the optical properties and the anomalous variation of the density, viscosity, and compressibility with the temperature. With rise of temperature, the colloidal molecules dissociate to a gradually increasing extent. In the colloidal form the water is supposed to have a smaller density and a greater compressibility than water which consists of simple molecules.

H. M. D.

Colloidal Chemistry of Caoutchouc. II. Theory of Vulcanisation. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 45—49).—It is pointed out that the apparently contradictory results obtained in connexion with experiments on the nature of the process of vulcanisation of caoutchouc by Henrichsen and Kindscher (this vol., i, 330) and by Bysow (*Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 281) may be due to the widely different sulphur concentrations which were used in the two series of experiments. Both series of experimental data are consistent with the theory that the sulphur is adsorbed according to an exponential formula.

Reference is also made to Reychler's experiments on the absorption of sulphur dioxide by caoutchouc (this vol., ii, 272). Although these experiments seem to show that the amount of absorbed sulphur dioxide is proportional to the pressure of the gas, the limits between which the pressure was varied are too narrow to refute the author's supposition that the absorption takes place in accordance with an exponential formula: $c = K.C^m$, in which m is nearly equal to unity.

H. M. D.

Certain Factors which determine the Constituents of Emulsions of Oil and Water. T. BRAILSFORD ROBERTSON (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 7—10).—When olive oil and water containing a little alkali hydroxide are thoroughly well shaken, an emulsion is obtained, the nature of which is dependent on the relative proportions of oil and water employed. When the relative quantities of the two substances are changed, the viscous, white emulsion of oil in water is at a particular (critical) point replaced by a much less viscous, yellow emulsion of water in oil. The author has investigated the influence of the concentration of the alkali hydroxide on the critical ratio. The experimental data indicate that above a certain limiting concentration the critical ratio is independent of the concentration of the alkali. The quantity of oil which can be emulsified by a given quantity of water diminishes as the concentration of the alkali hydroxide falls below this upper limiting value until, at a certain lower limiting concentration, the formation of a stable emulsion no longer takes place. The influence of the alkali on the nature of the emulsion formed is supposed to be due to its action on the free acid of the oil. When the amount of alkali in the aqueous layer is more than sufficient to neutralise the free acid, the critical ratio is unaltered. When the quantity of alkali is insufficient to neutralise more than a small proportion of the free acid, a stable emulsion cannot be formed.

H. M. D.

Appearance of a Maximum and Minimum Pressure with Heterogeneous Equilibria at a Constant Temperature. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 31—34).—The author discusses the conditions under which maximum and minimum pressures may occur in the equilibrium between the phases of a binary system at a given temperature. H. M. D.

Equilibrium in the System: Sulphuric Acid–Ammonium Sulphate–Water at 30°. G. C. A. van Dorp (*Zeitsch. physikal. Chem.*, 1910, **73**, 284—288).—The equilibria in the above system have been investigated by solubility measurements, and the results are represented on the usual triangular diagram. The solid substances in equilibrium with the different solutions are: $(NH_4)_2SO_4$; $[(NH_4)_2SO_4]_3,H_2SO_4$, and $(NH_4)HSO_4$. G. S.

Equilibria in the System: Sulphuric Acid–Lithium Sulphate–Water at 30°. G. C. A. van Dorp (*Zeitsch. physikal. Chem.*, 1910, **73**, 289—290. Compare preceding abstract).—Solubility measurements have shown that the three following compounds, Li_2SO_4,H_2O; Li_2SO_4, and $LiHSO_4$, exist in equilibrium with solutions of the components in different concentrations. G. S.

Chemical Affinity. The System $PbCO_3 + K_2CrO_4 = PbCrO_4 + K_2CO_3$. H. Golblum and G. Stoffella (*J. Chim. phys.*, 1910, **8**, 135—188).—The authors have determined the heat developed in the interaction of lead nitrate with potassium chromate in solution to be 10·58 Cal. per equivalent, from which the heat of formation of dissolved lead chromate is 15·23 Cal.

Since the action $PbCO_3 + K_2CrO_4 \longrightarrow PbCrO_4 + K_2CO_3 + 4\cdot98$ Cal. is exothermic, according to Berthelot's view, the mixture $[PbCrO_4 + K_2CO_3]$ should be the stable one. The product of the ionic solubilities of $[PbCO_3 + K_2CrO_4]$ is greater than the product of $[PbCrO_4 + K_2CO_3]$, hence, according to van't Hoff and Reicher's rule, the latter pair is the more stable.

The four salts cannot exist side by side in presence of their saturated solution, as they would form an invariant system. If the potassium salts are in excess, one of the lead salts, more usually the carbonate, disappears. The equilibrium diagram shows that at one particular concentration of potassium chromate (0·5679% at 25°) the solid residue may contain both lead salts together with potassium carbonate. Both lead salts should exist in contact with solutions in which a certain ratio of carbonate to chromate exists, but which are saturated with neither.

The ratio of dissolved carbonate to chromate in such solutions is the equilibrium constant of Guldberg and Waage. It is, however, not a constant ratio, but decreases with dilution on account of the disturbing effect of ionisation.

No compound or solid solution of potassium chromate and lead chromate is formed, but the solubility of potassium carbonate decreases as the amount of lead carbonate in the solid residue and in solution increases. A double compound of $K_2CO_3,PbCO_3$ appears to exist.

On adding lead nitrate solution to a mixed solution of potassium chromate and carbonate, the precipitation of lead chromate or carbonate does not take place in such a way as to produce the pre-determined ratio in the dissolved potassium salts. Whilst the interaction of lead carbonate and potassium chromate proceeds smoothly to an equilibrium, the interaction of lead chromate and potassium carbonate presents

periodic phenomena. The curve representing the amount of potassium chromate formed oscillates with decreasing amplitude until the equilibrium is finally attained. This is attributed by the author to the formation of a basic chromocarbonate of lead. On boiling lead chromate in potassium carbonate solution, an orthorhombic, ruby-red, crystalline solid is obtained with the composition: $3PbO,2CrO_3,2PbCO_3$.

R. J. C.

Ternary Systems with a Ternary Transition Point in the Liquidus-Solidus Diagram. The System Lead-Cadmium-Mercury. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1910, **73**, 328—342. Compare Abstr., 1907, ii, 870).—A general treatment of ternary systems is given, which differs somewhat from that already communicated, inasmuch as it was formerly assumed that more than three kinds of other substances could occur in the system. The statements are illustrated by the system lead–cadmium–mercury; the conclusions and the graphic representations of the equilibria do not differ greatly from those already given. A number of microphotographs illustrating the structure of the different alloys accompany the paper.

G. S.

Application of Thermal Analysis to Organic Chemistry. I. PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, **8**, 119—130. Compare Scheuer, this vol., ii, 470).—The formation of intermediate additive compounds in organic interactions has not received wider recognition on account of the rarity with which these compounds can be isolated. The author discusses the application of thermal methods, such as the study of the liquidus curve of interacting binary liquid mixtures, to this problem. The method has already been applied by Scheuer to elucidate the allied question of the influence of solvents on rotatory power. It is only applicable when the freezing points of the mixtures are considerably below the temperature at which action sets in, and it is interfered with by the formation of vitreous, amorphous solids. Heating curves and microscopical structure should afford valuable confirmation of the results. The actions hitherto studied have been such as require no catalyst or third substance, as this would necessarily complicate the reasoning.

R. J. C.

Molecular Compounds in Binary Organic Systems. A. WROCZYNSKI and PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, **8**, 189—221. Compare Guye, preceding abstract).—Liquidus curves have been determined at temperatures ranging from $+5°$ to $-112·5°$, using a double-walled apparatus like a Beckmann cryoscopic apparatus. The organic mixtures were cooled by placing the double-containing tube in a Dewar vessel containing solid carbon dioxide, ether, or liquid air, according to the case.

Benzyl chloride and anisole, which do not interact, gave perfectly normal liquidus curves. Benzyl chloride and methylaniline, which interact at room temperature, gave a broken f.-p. curve showing four compounds and four eutectics in the part studied. The compounds appear to contain benzyl chloride and methylaniline in the molecular ratios 3 : 1, 3 : 2, 2 : 1, 1 : 1.

Ethyl bromide and bromine appear to form an easily dissociated additive compound, $2EtBr,Br_2$, which is the parent substance of ethylene dibromide.

Ethyl acetate and aniline, which interact to give acetanilide, form at least three additive compounds at low temperatures, namely:

$CH_3\cdot CO_2Et,NH_2Ph$; $2CH_3\cdot CO_2Et,3NH_2Ph$; $CH_3\cdot CO_2Et,2NH_2Ph$.

Mixtures containing 20—40% of aniline are extremely viscous, so that perhaps a fourth compound containing 33—40% of acetate is also formed. Viscosity determinations of these mixtures at 0°, −9°, and −19·5° gave unbroken curves, from which no sure conclusion could be drawn. Pyridine and methyl iodide readily combine at room temperature, but there is no evidence of combination when they are brought together at −20°.

Ethyl ether and ethyl iodide form at a low temperature at least three compounds, presumably of the oxonium type, namely: $3EtI,OEt_2$; $2EtI,OEt_2$; EtI,OEt_2. The additive products in this case, however, dissociate into their original components, and no double decomposition can be shown to occur.

Chloroform and benzene do not combine, neither do benzene and nicotine. The last is confirmed by the very smooth curve of the rotatory power of nicotine in benzene solution. All the additive compounds observed are more or less dissociated, so that only approximate melting points were obtained for each. Mixtures rich in methylaniline or nicotine solidify to a vitreous mass with no true melting point. The same is true for the very viscous solution of 20—40% of aniline in ethyl acetate. R. J. C.

Dynamics of the Reaction between Alcohol and Sulphuric Acid. ROBERT KREMANN (*Monatsh.*, 1910, 31, 245—274).—The equilibrium represented by the equation

$$EtOH + H_2SO_4 \rightleftarrows EtSO_4H + H_2O$$

has been determined at different temperatures. In the first set of experiments the composition of the equilibrium mixture was determined gravimetrically, the unchanged sulphuric acid being precipitated by means of lead carbonate and the ethyl sulphuric acid determined in the filtrate. In this way it was shown that the reaction is not disturbed by the formation of ether or ethyl sulphate. The mean value of the equilibrium constant, $K = [\text{acid}][\text{alcohol}]/[\text{ester}][\text{water}]$, at 22°, 55°, 72°, and 96° is 1·74; it is independent of the temperature.

In the second set of experiments the equilibrium composition was determined by direct titration, the mean value being 1·70 at 40° and 51°.

Zaitschek (Abstr., 1898, ii, 19) in an investigation of the same equilibrium came to the conclusion that a constant could only be obtained on the assumption that the sulphuric acid present existed as the dihydrate. From a consideration of the melting-point curve of the system sulphuric acid–water, the author has calculated the degree of dissociation of sulphuric acid monohydrate, which would be the only one present at the concentrations used, at different temperatures, and finds that the values of K, calculated on the assumption that this

hydrate is present, are not so good as when hydrate formation is neglected.

The velocity of decomposition of ethyl sulphuric acid in water was measured at 55° and 66°, and found to be approximately proportional to the concentration of the hydrions. The reaction is autocatalytic, but since sulphuric acid is formed as a product of reaction, the concentration of the hydrions remains approximately constant, and the velocity equation simplifies to one of the first order. The constants are satisfactory at the commencement of the reaction, but diminish slightly as the reaction proceeds. The temperature-quotient is abnormally high, namely, 4·5.

The velocity of formation of ethyl sulphuric acid from different mixtures of alcohol and sulphuric acid was measured at 40° and 51°. From the results the velocities of the direct and inverse reactions could be calculated in the usual manner. With increasing concentration of sulphuric acid these velocities go through a weakly-defined minimum, after which they rapidly increase. The latter increase cannot be explained by the increase in the hydrion concentration alone; it must be due to secondary causes, as, for example, hydrate formation, which may have considerable influence kinetically, although it plays no part in the equilibrium.

These two velocities in systems which are initially free from water are about fifty times greater than in aqueous solutions; in 50% alcohol they are slightly greater than in water. In all cases the temperature-quotient is greater than 2. T. S. P.

Quaternary and Quinternary Systems: The System Alcohol, Ether, Water, Sulphuric Acid, and Ethyl Sulphuric Acid at 0°. ROBERT KREMANN (*Monatsh.*, 1910, 31, 275—284).—The experimental figures, together with a graphical representation of the same, of the following systems at 0° are given. Ternary: (1) ether–water–alcohol; (2) ether–water–sulphuric acid. Quaternary: (1) ether–water–alcohol-sulphuric acid; (2) ether–water–alcohol–ethyl sulphuric acid. Quinternary: ether–water–alcohol–ethyl sulphuric acid–sulphuric acid. T. S. P.

Equilibrium between Ammonium Benzoate, Benzamide, and Water. E. EMMET REID (*Amer. Chem. J.*, 1910, 44, 76—80).—At temperatures between 180° and 220° equilibrium is attained from either side in the reaction represented by the equation $C_6H_5 \cdot CO_2NH_4 \rightleftarrows C_6H_5 \cdot CO \cdot NH_2 + H_2O$ when the system contains about 25% of ammonium benzoate. C. S.

Phase Rule. R. BOULOUCH (*J. Chim. phys.*, 1910, 8, 113—118).—The phase rule can be deduced from the postulate that equilibrium is independent of the masses of the phases.

The independent components c in a system, distributed amongst ϕ phases of masses $\mu_1, \mu_2, \mu_3 \ldots$, have masses $A, B, C \ldots$, which obey c distribution equations of the form $A = \mu_1 a_1 + \mu_2 a_2 + \mu_3 a_3 + \ldots$.

The total volume of the system is $V = \mu_1 v_1 + \mu_2 v_2 + \mu_3 v_3 + \ldots$, where $v_1, v_2, v_3 \ldots$ are the specific volumes of the phases.

If $c > \phi$, $(c - \phi)$, independent sets of distribution equations give different values for $\mu_1, \mu_2, \mu_3 \ldots$. Equilibrium can also be modified by temperature and pressure. The degrees of freedom are therefore $(c - \phi + 2)$, that is, the system is multivariant.

If $c = \phi$, the variance $(c - \phi + 2) = 2$, that is, the system is bivariant. Temperature and pressure alone are variables, since the volume is completely defined by the values given to $\mu_1, \mu_2, \mu_3 \ldots$.

If $c = (\phi - 1)$, the ϕ masses $\mu_1, \mu_2, \mu_3 \ldots$ can be determined by the $(\phi - 1)$ distribution equations in conjunction with the volume equation, arbitrarily fixing a value for V. Pressure will be a function of temperature in this case, so that the system is univariant.

If $c = (\phi - 2)$, a solution is only obtainable by reducing the number of unknowns by arbitrarily fixing one of them, μ_x. The system is consequently invariant.

When the c equations are such that complete solution of $\mu_1, \mu_2, \mu_3 \ldots$ cannot be obtained from any set of ϕ of them, one of the quantities, μ, may be arbitrarily fixed when the remaining $(\phi - 1)$ follow as functions of it. $(c - \phi + 1)$ sets of solutions are thus obtainable.

The volume in each case becomes a function of the arbitrarily fixed μ, so that $p = f(t)$, and the condition is that of an indifferent point.

R. J. C.

Is the Hydrolysis of Cane Sugar by Acids a Unimolecular Reaction when Observed with a Polariscope? C. S. Hudson (*J. Amer. Chem. Soc.*, 1910, **32**, 885—889).—Polemical. A reply to Julius Meyer (Abstr., 1908, ii, 265; 1910, ii, 403). T. S. P.

Hydrolysis of Esters of Halogen-substituted Acids. W. A. Drushel and J. W. Hill (*Amer. J. Sci.*, 1910, [iv], **30**, 72—78).—The esters of chloro- and bromo-acetic acids show no tendency to decompose with liberation of halogen in aqueous solutions of hydrochloric and hydrobromic acid, but from the corresponding iodo-esters in hydriodic acid solution iodine is set free.

The rate of hydrolysis of a number of alkyl chloro- and bromo-acetates (in $N/20$-solution when sufficiently soluble) in the presence of hydrochloric and hydrobromic acids respectively have been measured at 25° and 35°. The rate of hydrolysis is lowered by the introduction of halogen; the relative velocities for acetic, chloroacetic, and bromoacetic esters is 33 : 21 : 25. The rates of hydrolysis of different esters of the same acid are in very close agreement.

The temperature-coefficient of the catalytic activity of $N/20$-hydrochloric acid is 2·0 between 25° and 35°, and 3·0 between 25° and 40°; the corresponding value for $N/20$-hydrobromic acid is 1·7 between 25° and 35°. G. S.

Simultaneous Reactions in the Decomposition of Ethyl Diazoacetate. Hilary Lachs (*Zeitsch. physikal. Chem.*, 1910, **73**, 291—327. Compare Fraenkel, Abstr., 1907, ii, 746).—It was observed by Fraenkel (*loc. cit.*) that when ethyl diazoacetate undergoes catalytic decomposition to ethyl glycollate in the presence of an acid, such as hydrochloric or nitric acid, the acid is used up in a simultaneous

reaction, resulting in the formation of ethyl chloroacetate or nitroacetate. This point has now been further investigated.

The rates of the two simultaneous reactions have been measured at 15° in 50% alcohol by determining the change of conductivity and the rate of liberation of nitrogen. As catalysts, hydrochloric and nitric acids, in the presence of varying concentrations of the corresponding alkali salts, were used. The acids disappear the more rapidly and the nitrogen liberated is the less in amount, the greater the concentration of the Cl′ and NO_3' ions. With constant hydrogen ion concentration and varying Cl′ or NO_3' ion concentration respectively, the amount of nitrogen liberated is independent of the ester concentration, and depends only on that of the anions. When the liberation of nitrogen has ceased, the double esters (ethyl nitroacetate or ethyl chloroacetate) are only stable in such solutions as contain free NO_3' or Cl′ ions.

An equation containing the ratio of the velocity-coefficient of the decomposition of ethyl diazoacetate, k_e, to that of the formation of the double ester, k_d, is deduced, and is shown to represent the experimental results satisfactorily. From this ratio and the known value of k_e, the rates of formation of the double esters are obtained. The rate of formation of ethyl nitroacetate is proportional to the 2/3 power of the NO_3' concentration, that of ethyl chloroacetate to the 4/5 power of the Cl′ ion concentration. Under corresponding conditions, the rate of formation of ethyl chloroacetate is about ten times that of the corresponding nitro-ester. G. S.

Nature of Neutral Salt Action. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1910, **73**, 269—283).—In a previous paper (Abstr., 1907, ii, 238) the author has shown that whilst carbon dioxide has very little effect on methyl-orange in water alone, it changes the colour of the indicator to red in the presence of a neutral salt, such as sodium chloride. Veley (*Zeitsch. physikal. Chem.*, 1908, **61**, 464) has suggested that this is due to hydrogen ions liberated from the salt by the action of carbonic acid, but this is now shown to be untenable; the total hydrogen ion concentration is greater in a solution of carbon dioxide in water alone than when sodium chloride is present. The sensitiveness of methyl-orange to hydrochloric acid is not affected by potassium chloride in normal solution, but still greater concentrations exert some action.

In order to produce the same tint in corresponding solutions of potassium sulphate and of potassium chloride containing methyl-orange, over six times as much hydrochloric acid must be added to the former solution as to the latter: a result ascribed to some interaction between methyl-orange and SO_4 ions.

The bearing of neutral salt action on the deviations from Ostwald's dilution law is discussed. G. S.

Apparent Chemical Attractions. RAPHAEL E. LIESEGANG (*Ann. Physik*, 1910, [iv], **32**, 1095—1101. Compare Abstr., 1906, ii, 218).—Further observations are described relating to what appears to be chemical action at a distance. If two drops of a sodium hydroxide

solution are placed at a short distance from one another on a gelatin film containing citric acid and coloured red by the addition of litmus, it is found that the rate of movement of the line of separation of the red and blue regions is considerably greater on the sides of the drops which face each other than on the opposite sides. The fact that this behaviour is the same as that previously observed when drops of silver nitrate were placed on a gelatin film containing sodium chloride indicates that the phenomenon is not connected in any way with the formation of precipitation membranes. The effect is supposed to be due to the more rapid removal of the acid from the region between the drops of the alkali solution. H. M. D.

The Shape of the Atom. R. D. KLEEMAN (*Phil. Mag.*, 1910, [vi], 20, 229—238).—Various consequences are discussed in which the shape of the atom is assumed to be spherical. The sum of the cross-sectional areas of molecules as calculated from this assumption is compared with that found from the kinetic theory for gases at 0°. The gases examined fall into three groups, for each of which an approximately constant ratio between the theoretical and experimental quantities holds. The differences for different groups are ascribed to differences in the arrangements of the atoms and in the amount of external space included in the molecules. Further deductions are made of the coefficients of diffusion of one gas into another, but only a rough approximation between the calculated and experimental values is obtained. It is further pointed out that the mean angle of distribution of secondary β-rays from the direction of the primary β-rays producing them will depend less on the nature of the atom the greater its atomic weight. The results of Bragg and Madsen (Abstr., 1909, ii, 112) on the ratio of the amounts of secondary β-radiation from the two sides of a thick plate penetrated normally by γ-rays are cited as being in agreement with this deduction.

F. S.

Continuous Absorbing Column. MAURICE BILLY (*Bull. Soc. chim.*, 1910, [iv], 7, 579—583).—An apparatus is described for the purification, desiccation, or quantitative absorption of gases. In principle it depends on the washing of the gas by a suitable liquid descending over glass balls, contained in a glass tube through which the gas ascends. A reservoir of special form is described, which gives a continuous and regulated flow of the washing liquid, and the removal of the latter after use is provided for by a safety tube of special form. The apparatus is automatic in use, and can be evacuated or cleaned without being dismounted. T. A. H.

Separating Apparatus. C. A. JACOBSON and S. C. DINSMORE (*Amer. Chem. J.*, 1910, 44, 84—85).—The apparatus consists of a double-bulbed separating funnel attached by means of a cork in the neck to a pipette siphon. Its advantages are: (i) better and more rapid extraction; (ii) emulsions are not formed so readily; (iii) the upper of two liquids can be siphoned off almost completely when the surface of separation of the two liquids is situated at the constriction

between the two bulbs ; (iv) the middle layer of three liquids can be siphoned off without disturbing the other two. C. S.

The Acetylene Lamp. [Lecture Experiment.] NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], **82**, 183—185).—A description of an acetylene lamp made entirely of glass, so that the working parts can be seen. T. S. P.

Cooling of Flames. [Lecture Experiments]. NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], **82**, 185—188).—A description of slight modifications of the ordinary experiments showing the action of wire gauze on flames. T. S. P.

The Striking-Back of the Bunsen Flame. [Lecture Experiment.] NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], **82**, 189—192).—A description of some experiments to illustrate the striking-back of the Bunsen flame. T. S. P.

Inorganic Chemistry.

Presence of Metals and Metalloids in Drinking Waters. Practical Consequences. FELIX GARRIGOU (*Compt. rend.*, 1910, **150**, 1374—1375. Compare this vol., ii, 549).—Most drinking waters contain traces of metals. The author's method of detecting metals of groups III, IV, V, and VI has been applied to more than 2,000 samples, particularly from the Pyrennean basin. A survey of the results shows that the analysis of mineral waters or even drinking waters will often simplify the mineralogical study of a district. The method is particularly useful in revealing metallic lodes. R. J. C.

Oxygenated Compounds of Fluorine. GINO GALLO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 753—755. Compare this vol., ii, 405). —The author has repeated his former experiments, taking additional precautions to exclude the possibility of the presence of hydrogen in the fluorine used, but in this case also a violent explosion occurred four or five minutes after the commencement. Some solid potassium hydroxide which had been introduced into the apparatus did not give any indication of the presence of oxygenated fluorine compounds when examined after the explosion. R. V. S.

Action of Hydrogen on Sulphur Monochloride and Thionyl Chloride under the Influence of the Silent Electric Discharge. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, **150**, 1752—1754).—On submitting sulphur monochloride to fractionation under atmospheric pressure, partial decomposition occurred with production of sulphur dichloride and sulphur. The monochloride is completely reduced by hydrogen under the influence of the silent electric

discharge. Under the same conditions, thionyl chloride undergoes reduction in accordance with the equation: $4SOCl_2 + 3H_2 = S_2Cl_2 + 2SO_2 + 6HCl$; sulphur is also formed through the action of hydrogen or sulphur dioxide on the monochloride, whilst sulphuryl chloride is also formed, according to the reaction: $2SO_2 + 3S_2Cl_2 = SO_2Cl_2 + 2SOCl_2 + 5S$. In the absence of the discharge, sulphur dioxide slowly reacts with sulphur monochloride at 160—170°, giving sulphuryl chloride and sulphur. W. O. W.

Synthesis of Caro's Acid and of Persulphuric Acid. JOH. D'ANS and W. FRIEDERICH (*Ber.*, 1910, 43, 1880—1882).—In order to prepare Caro's acid, chlorosulphonic acid is well cooled and the calculated quantity of 100% hydrogen peroxide (compare Ahrle, Abstr., 1909, ii, 395) slowly added. When the evolution of hydrogen chloride has ceased, the reaction mass is slowly allowed to become warm, and the dissolved hydrogen chloride sucked off at the pump. The residue then solidifies to a crystalline mass, m. p. about 45°, which can be kept for some days. It consists of Caro's acid, and the synthesis confirms the formula $HO{\cdot}SO_2{\cdot}O{\cdot}OH$.

When treated with another molecule of chlorosulphonic acid, Caro's acid is transformed into persulphuric acid, $H_2S_2O_8$. The reaction is best carried out by mixing the calculated quantities of hydrogen peroxide and chlorosulphonic acid, and proceeding as in the preparation of Caro's acid. Crystals of persulphuric acid are obtained, m. p. a little above 60° (decomp.), which can be kept for months. When dissolved in water, it is hydrolysed to a considerable extent into Caro's acid and sulphuric acid.

The authors confirm the formation of perphosphoric acids from hydrogen peroxide (100%) and phosphoric oxide or metaphosphoric acid (compare this vol., ii, 498).

Acetyl chloride gives acetyl peroxide when treated with 100% hydrogen peroxide. T. S. P.

Equations and Tables for Saturated and Superheated Nitrogen Vapour. RUDOLPH PLANK (*Physikal, Zeitsch.*, 1910, 11, 633—643).—The available pressure, volume, and thermal data for nitrogen at low temperatures have been collected and analysed. Tables are given in which the values of various factors are recorded for each 1° between −210° and −182°. These factors include the vapour pressure of the liquid, the specific volume of the liquid and of the saturated vapour, the heat content and the entropy of liquid and vapour, the latent heat of vaporisation, and the specific heat of the vapour. The pressure, volume, and temperature data for the unsaturated vapour can be represented by $v = 30{\cdot}2T/p - 64{\cdot}4/T^2$; the specific heat by $C_p = 0{\cdot}2246 + 0{\cdot}000038T + 0{\cdot}905P/T^3$. The pressure of the saturated vapour corresponds with the equation $\log p = 3{\cdot}0 + 0{\cdot}4\log T - 289{\cdot}6/T$, and the latent heat of vaporisation varies with the temperature according to $r = 68{\cdot}85 - 0{\cdot}2736T$. H. M. D.

Preparation of Anhydrous Hydrazine. F. RASCHIG (*Ber.*, 1910, 43, 1927).—Contrary to the usual statements in the literature, anhydrous hydrazine may be obtained from hydrazine hydrate by

treatment with sodium hydroxide. One hundred grams of ordinary sodium hydroxide, in pieces as big as a pea, are added to 100 grams of hydrazine hydrate contained in a distilling flask with long side-tube. The flask is heated in an oil-bath in such a way that the temperature takes two hours to rise to 113°, the boiling point of hydrazine. By this time all the sodium hydroxide will have dissolved, and the temperature of the bath can be further raised to 150°. Anhydrous hydrazine distils over, in almost theoretical quantity, as a strongly fuming liquid, and can be collected in a dry stoppered bottle. It keeps quite well in the bottle, and the stopper does not stick, even on keeping for a long time.

During the distillation, the vapours must not come into contact with cork or rubber, and care must be taken not to inhale them. T. S. P.

Chemical Action of High Pressure. Compression of Nitrous Oxide and a Mixture of Nitrogen and Hydrogen; Decomposition of Carbon Monoxide by Pressure. E. BRINER and A. WROCZYNSKI (*Compt. rend.*, 1910, **150**, 1324—1327. Compare this vol., ii, 557).—Nitrous oxide is more stable than nitric oxide, and appears to require a higher temperature to cause any appreciable decomposition. When submitted to a pressure of 600 atmospheres at 420°, it suffers a slight decomposition with increase in volume.

Nitrogen and hydrogen do not combine when subjected to 900 atmospheres at the ordinary temperature, although Haber has recently obtained ammonia by the combined action of temperature, pressure, and a catalyst.

Carbon monoxide when compressed under 800 atmospheres at the ordinary temperature does not change, but when compressed under 600 atmospheres at 320° undergoes a decomposition with diminution in volume, amounting to 10% in twenty hours. The author points out that the equation $2CO \longrightarrow CO_2 + C + 38{\cdot}7$ Cal. is exothermic, so that decomposition might be expected. Carbon dioxide was found to be present (5·5% in one case), and a slight greyish-black deposit, perhaps carbon, was noticed. It is suggested that a lower oxide of carbon may have been formed, as Berthelot supposed (compare, however, Gautier, this vol., ii, 605).

The chemical action of high pressures is in favour of the view that catalysis in gases results from the condensing action of the catalytic surface. R. J. C.

Nature of the Product Described as Black Phosphorus. DÉSIRÉ GERNEZ (*Compt. rend.*, 1910, **151**, 12—16).—The conversion of phosphorus into a black substance by contact with mercury (Thénard, 1812) was supposed by Blondlot (*Compt. rend.*, 1865, **60**, 830; 1870, **70**, 836) to be due to the formation of an allotropic modification of phosphorus. The present author describes experiments which appear to show that molten phosphorus is capable of dissolving small quantities of mercury, forming a colourless solution. Such a solution remains colourless when in a state of superfusion, but becomes black, through precipitation of mercury, if caused to solidify. Salts of mercury bring about the same phenomenon, through reduction to the metallic state. W. O. W.

Preparation and Molecular Weight of Hypophosphoric Acid. ARTHUR ROSENHEIM and JACOB PINSKER (*Ber.*, 1910, **43**, 2003—2014).—Hypophosphoric acid is best prepared by a modification of Corne's method, (Abstr., 1882, 1264) as follows: To 100 grams of copper turnings, contained in a 3-litre flask, are added 100 c.c. of water and 200 c.c. of nitric acid (D = 1·4). When the reaction is moderated somewhat, stick phosphorus is gradually added until all the copper has been precipitated as a mixture of copper phosphide and spongy copper, the temperature being maintained between 50° and 70°. The clear, colourless liquid is then decanted off, and half of it neutralised with sodium carbonate; after the addition of the remaining half, sodium hypophosphate, $NaHPO_3 + 2H_2O$, separates after a time, the yield being about 10% of the theoretical.

Silver nitrate (compare Abstr., 1883, 1052) does not give such good results as copper nitrate. Zinc, manganese, nickel, cobalt, mercuric and ferric nitrates do not give rise to the formation of hypophosphoric acid, neither do the oxides of nitrogen. When, however, the phosphides of copper, nickel, or silver are used as anodes in 1—2% sulphuric acid, the voltage being 3—10, hypophosphoric acid is produced, in some cases yields as high as 60% being obtained. Iron phosphide produces phosphoric acid only.

Hypophosphoric acid gives a characteristic *guanidine* salt,

$$(CH_5N_3)_4,H_2PO_3,5H_2O;$$

white, shining needles, which are soluble in water to the extent of 1·038 grams in 100 c.c. of solution at 28·5°. The solution is strongly alkaline. The other acids of phosphorus do not form similar salts.

Benzyl hypophosphate, $(C_7H_7)_2PO_3$, was obtained as a yellow oil, which could not be distilled, by the interaction of benzyl iodide and silver hypophosphate. The molecular weight in ether was 239—245.

Cryoscopic determinations of the molecular weight of hypophosphoric acid in aqueous solution (compare this vol., ii, 121) point to the formula $H_4P_2O_6$, but the authors believe that this is due to association of the simpler molecules H_2PO_3, for the following reasons: the molecular conductivity of aqueous solutions is abnormally high if the formula is taken as $H_4P_2O_6$, and the figures so obtained ($\mu = 367·4$ for $v = 31·6$; $\mu = 608·8$ for $v = 1111·2$) are not in accordance with the properties of hypophosphoric acid. Moreover, the molecular conductivity can only be brought into line with the molecular conductivities of the other acids of phosphorus when the formula is taken as H_2PO_3.

Hypophosphoric acid reacts as a monobasic acid when methyl-orange is used as indicator; with phenolphthalein as indicator, 2 mols. of H_2PO_3 are neutralised by 3 mols. of sodium hydroxide.

Hypophosphoric acid monohydrate, H_2PO_3,H_2O, forms rhombic crystals [$a : b : c = 0·5635 : 1 : ca.\ 1·7$]. T. S. P.

Action of Hydrogen on Carbon Monoxide; Formation of Water and Methane. Action of Water at a Red Heat on Carbon Monoxide. Applications to Volcanic Phenomena. ARMAND GAUTIER (*Compt. rend.*, 1910, **150**, 1564—1569. Compare Abstr., 1906, ii, 538).—Hydrogen begins to exert a reducing action on carbon monoxide at 400°, water, carbon dioxide, and a little methane

being formed. The reaction is a balanced one, the production of water reaching a maximum at about 1200°. At 900—1000° the amounts of water vapour and carbon dioxide formed are in agreement with the equation $4CO + 2H_2 = 2H_2O + CO_2 + 3C$; the formation of carbon, however, is not usually observed unless an excess of hydrogen is employed. When a mixture in the proportions $CO + 3H_2$ was passed through a porcelain tube at 900°, the reaction appeared to be represented as $3CO + H_2 = H_2O + CO_2 + C_2$; but in a second experiment, under apparently identical conditions, no carbon was deposited, the volumes of gaseous products agreeing with the equation $4CO + 8H_2 = 2H_2O + CO_2 + 3CH_4$.

The amount of methane formed increases with the proportion of hydrogen, and depends on the rapidity with which it is removed from the sphere of action. Traces of formaldehyde were detected at 450—650°, but not above 950°.

The author's earlier experiments on the action of carbon monoxide on water vapour at a red heat, have been repeated, and traces of formaldehyde detected amongst the products at 550° and 800°.

The foregoing reactions are considered to throw light on the occurrence of water, oxides of carbon, methane, and hydrogen in volcanic gases. W. O. W.

Action of Iron and Its Oxides on Carbon Monoxide at a Red Heat; Application to Geological Data. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1910, **151**, 16—22. Compare this vol., ii, 607).—The authors have repeated and extended the work of earlier observers on the reduction of carbon monoxide by iron at a red heat.

The production of carbon appears to take place in accordance with the equation: $3Fe + 28CO = Fe_3O_4 + 16C + 12CO_2$. The black solid resulting from prolonged action of the gas can be separated by a magnet into two parts, the more magnetic consisting of a mixture of carbides of iron, whilst the residue is carbon with traces of iron. Two carbides approximating in composition to $Fe_{12}C$ and Fe_5C have been separated by taking advantage of the greater readiness with which the former dissolves in sulphuric acid. The reaction is represented as $Fe_{12}C + 12H_2SO_4 = 12FeSO_4 + CH_4 + 10H_2$. The carbide Fe_5C also yields methane, hydrogen, and probably small quantities of cyclic hydrocarbons when treated with sulphuric acid.

The product of the action of carbon monoxide on iron is attacked by steam at a red heat with production of hydrogen, methane, carbon dioxide, and traces of formaldehyde. W. O. W.

Isotherms of Monatomic Gases and of their Binary Mixtures. IV. Preparation of Argon. V. Vapour Pressures above $-140°$, Critical Temperature, and Critical Pressure of Argon. C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 54—65).—The methods employed for the separation and purification of argon have been examined.

Metallic calcium combines with nitrogen at a low red heat, but the reaction takes place too slowly for use on a large scale. Much better

results are obtained with a mixture of 90% of calcium carbide and 10% of calcium chloride, and this method is recommended for the preparation of large quantities of crude argon. For the final purification a mixture of twenty parts by weight of calcium oxide, four of magnesium, and one of sodium was found to give good results. The removal of the last traces of nitrogen by combining it with oxygen under the influence of an electric discharge is more conveniently effected by means of an arc between platinum electrodes than by the use of a spark discharge.

Argon can be separated from the small quantities of neon which it contains by fractional distillation at the temperature of liquid oxygen.

Measurements of the vapour pressure and critical data of argon gave the following results, after correction for the small quantities of inpurities which the examined gas contained :

Temperature	$-140·8°$	$-134·72°$	$-129·83°$	$-125·49°$	$-122·70°$	$-122·49°$
Pressure in atmos. ...	22·185	29·264	35·846	42·457	47·503	47·890

Critical temperature $= -122·44°$; critical pressure $= 47·996$ atmospheres.

H. M. D.

Sodium Manganate and its Hydrates. VICTOR AUGER (*Compt. rend.*, 1910, **151**, 69—70).—Sodium manganate, Na_2MnO_4, is easily prepared as follows : Sodium permanganate is heated in a silver or platinum dish with twice the calculated quantity of sodium hydroxide. Oxygen begins to be evolved at 115°, and the reaction is complete at 125°. On cooling, the anhydrous manganate separates in black crystals showing a violet reflex. The substance is stable below 170°, but at this temperature loses oxygen, forming a manganimanganate. A solution containing excess of sodium hydroxide deposits large, black prisms of the hydrate, $Na_2MnO_4,6H_2O$.

The hydrate, $Na_2MnO_4,4H_2O$, resembles the foregoing, and separates from solutions containing 5% of sodium hydroxide. When cooled in a freezing mixture the aqueous solution yields the salt,

$$Na_2MnO_4,10H_2O,$$

as black needles, m. p. 17° ; these appear to be isomorphous with sodium chromate. W. O. W.

Solubility of Silver Sulphate in Alkali Sulphates. BARRE (*Compt. rend.*, 1910, **150**, 1321—1324).—The solubility of silver sulphate in presence of potassium sulphate and ammonium sulphate increases as the amount of alkali sulphate increases. The same is true of sodium sulphate below its transition point (33°). Above 33° the solubility of silver sulphate rises to a maximum at a certain concentration of sodium sulphate dependent on the temperature. The solid residue contains, not only silver sulphate, but sodium sulphate, the percentage of which increases with its concentration in the liquid phase. Mixed crystals are therefore produced.

The solubility curves for various temperatures all end at a concentration, 40% sodium sulphate, that is, the mixed crystals formed

at this concentration are equally soluble at all temperatures, and have therefore no heat of dissolution. Mixed crystals with more silver salt dissolve exothermally, and increase in solubility with temperature, like pure silver sulphate; mixed crystals with more sodium sulphate dissolve endothermally, and decrease in solubility with temperature like sodium sulphate. R. J. C.

The Solubility Influence of Electrolytes. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **67**, 365—368. Compare this vol., ii, 192, 407).—The solubility of barium hydroxide is increased by the presence of alkali chlorides, the effect being greatest with lithium chloride, and least with rubidium chloride. The solubility of cupric sulphate is increased by the presence of sodium and potassium and rubidium chlorides, but depressed by that of lithium chloride. In both cases the order is that of the electro-affinities of the cations. Double salts and complex ions must be formed. C. H. D.

The Phosphates of Calcium. IV. FRANK K. CAMERON and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1910, **32**, 869—873).—Owing to the confusion regarding the relative stability of the hydrated and the anhydrous dicalcium phosphate, the equilibria existing in the system $CaO-P_2O_5-H_2O$, at 25°, have been further investigated. Solutions of phosphoric acid of varying concentration were prepared, and to each solution weighed quantities of potassium chloride and of tricalcium phosphate in sufficient quantity to give a permanent precipitate were added. After equilibrium had been attained, the composition of the solution and of the solid phase was determined. The potassium chloride was added, so that Bancroft's "tell-tale" method (Abstr., 1905, ii, 685; 1909, ii, 147) for determining the composition of the solid phase could be employed.

The composition of the solid phases was found to be $CaHPO_4,2H_2O$ and $CaH_4(PO_4)_2,H_2O$, with a region between, which was not explored, where the composition of the solid phase was probably $CaHPO_4$. This result is in accordance with Bassett's last determination (Abstr., 1908, ii, 675) of the transition interval of $CaHPO_4,2H_2O \rightleftarrows CaHPO_4 + 2H_2O$, but is not in accord with his direct determination of the composition of the solid phases.

The presence of potassium chloride in solutions containing calcium oxide and phosphoric oxide increases slightly the lime content of solutions in equilibrium with dicalcium phosphate and monocalcium phosphate. T. S. P.

Initial Temperatures at which Oxides of Metals Give Up Oxygen to Reducing Gases. IRVING W. FAY, ALBERT F. SEEKER, FREDERICK H. LANE, and GEORGE E. FERGUSON (*Polytechnic Engineer*, 1910, **10**, 72—79).—The authors have submitted a number of metallic oxides to the action of hydrogen, carbon monoxide, ammonia, and methane at various temperatures for a period of six hours, and have ascertained the lowest temperatures at which the oxides begin to lose oxygen. The following results were obtained:

Oxide.	CO.	H_2.	NH_3.	CH_4.
Au_2O_3 …………	0° and below	0° and below	—	—
Ag_2O …………	0	0	—	—
Hg_2O …………	0	80	67°	220°
HgO (yellow)…	0 and below	50	—	—
HgO (red) ……	90	115	157	200—210
Pb_2O …………	—	—	202	202
PbO_2 …………	110	150	198	45
Pb_3O_4 …………	150	170	above 300	158
PbO……………	160	190	299	210
CuO …………	75	125	225	280
Cu_2O …………	—	—	208	230
CdO……………	140	—	—	—
ZnO…………	170	—	233	152—159
As_2O_3 …………	60	—	—	—

The Action of Hydrogen Sulphide on White Lead. Julius F. Sacher (*Chem. Zeit.*, 1910, 34, 647—648).—Hydrogen sulphide is practically without action on lead carbonate, and carbon dioxide is not evolved during the blackening of white lead. The amount of sulphur taken up by white lead is always less than that required to convert the whole of the lead hydroxide into sulphide, even when the reaction is made as complete as possible. In order to avoid secondary reactions, the white lead is mixed with alcohol, which is then saturated with hydrogen sulphide and removed by evaporation. The analyses agree well with the formula $4PbCO_3,PbS,Pb(OH)_2$, which may be written: $S(Pb{\cdot}CO_3{\cdot}Pb{\cdot}CO_3{\cdot}Pb{\cdot}OH)_2$.

At 85—90°, in presence of water, the whole of the lead hydroxide is converted into sulphide, a little of the carbonate being also converted, owing to previous hydrolysis. Lead sulphate is only blackened in presence of water, owing to hydrolysis; pure lead sulphate in alcohol is unchanged by hydrogen sulphide.

Blackened white lead is not decolorised by light in the absence of moisture. C. H. D.

Purification of Mercury. C. J. Moore (*Chem. Zeit.*, 1910, 34, 735).—In the Lothar-Meyer apparatus for the purification of mercury by letting it fall in fine drops through dilute nitric acid, the author replaces the funnel drawn out to a fine point by a tube shaped like an inverted thistle funnel. Over the mouth of the funnel is fastened a piece of chamois leather, and the mercury is pressed through this to fall in a fine shower through the nitric acid. The stem of the thistle funnel contains a side-tube connected with the reservoir of mercury by means of rubber tubing and a screw-clip; the end of the stem is also closed by means of rubber tubing and clip. Eight % nitric acid is recommended for use in the apparatus. T. S. P.

The Action of Ammonia on Mercurous Chloride. Haridas Saha and Kumud Nath Choudhuri (*Zeitsch. anorg. Chem.*, 1910, 67, 357—360).—"Black precipitate" consists of a mixture of metallic mercury with infusible white precipitate. The latter substance is soluble in concentrated ammonia, and crystallises when the solution is

allowed to evaporate in a vacuum over sulphuric acid. After drying at 100°, the crystals have the composition NH_2HgCl. It is impossible to assign a formula to the black precipitate, as a part of the white compound contained in it goes into solution, according to the concentration of the ammoniacal liquid. C. H. D.

The So-called Euxenite Earths. OTTO HAUSER and FRITZ WIRTH (*Ber.*, 1910, **43**, 1807—1812. Compare this vol., ii, 47).—The authors have investigated a number of zirconium minerals in order to see if the zirconia was accompanied by a strange earth, as has been supposed to be the case by Hofmann and Prandtl (Abstr., 1901, ii, 387).

The minerals investigated were zircon, wöhlerite, uhligite, eudialyte, basalt, elaeolite-syenite, sodalite-syenite, katapleiite, mosandrite, and natural zirconia. In each case, zirconium hydroxide was obtained from the mineral in an approximately pure condition by the usual methods. This zirconium hydroxide should contain the strange earth, if present. It was therefore fractionated by transformation into the sulphate and hydrolysis of the aqueous solution by boiling, whereby about half the zirconium is precipitated as the basic sulphate (Abstr., 1907, ii, 626). Each of the fractions was examined spectroscopically, and also the equivalent determined. In no case were indications of the presence of a strange earth obtained. T. S. P.

Basic Nitrate of Yttrium. CHARLES JAMES and L. A. PRATT (*J. Amer. Chem. Soc.*, 1910, **32**, 873—879).—In order to study the system Y_2O_3–N_2O_5–H_2O, it was necessary to prepare a large amount of pure yttrium oxide, since yttrium nitrate is extremely soluble. To this end, crude yttria earths were first submitted to a long fractional crystallisation by the bromate method (Abstr., 1908, ii, 190, 498). The middle fractions, containing the yttrium, together with a little erbium and holmium, were then precipitated as the hydroxide, which was further converted into the nitrate. The nitrate was then submitted to fractional decomposition, this being carried out by evaporating the solution and fusing the residue until a portion had decomposed. After forty such operations, an yttrium nitrate was obtained of such purity that a layer 12·5 cm. thick of the saturated solution was perfectly colourless, and showed only very faint bands of erbium and holmium.

The equilibrium relations were studied by shaking up solutions of yttrium nitrate of varying concentrations with excess of yttrium oxide at 25°. Equilibrium was attained after four and a-half months, after which time the compositions of the various solid phases and solutions were determined.

The only basic nitrate which exists at 25° has the formula $3Y_2O_3,4N_2O_5,20H_2O$. It is stable in air, and can exist in contact with water containing more than 33 grams of yttrium nitrate to 100 grams of water.

At 25°, 141·6 grams of yttrium nitrate dissolve in 100 grams of water. T. S. P.

Scandium. II. Sir William Crookes (*Phil. Trans.*, 1910, **210**, *A*, 359—386; *Proc. Roy. Soc.*, 1910, *A*, **84**, 79—85. Compare Abstr., 1908, ii, 695; 1909, ii, 44).—The preparation and properties of a further number of scandium salts are described. In the majority of cases the salts were prepared by dissolving scandium hydroxide in the acid, or by double decomposition between scandium nitrate and a salt of the acid.

Scandium iodate, $Sc(IO_3)_3$, when washed and dried in the air, is a white, crystalline powder containing $18H_2O$. Under varying conditions of dehydration, hydrates with 15, 13, and $10H_2O$ have been obtained, and the salt becomes anhydrous on heating at 250°. The *sulphite*, $Sc_2(SO_3)_3$, is anhydrous, and practically insoluble in cold water; the *borate*, $ScBO_3$, prepared by fusing together scandium oxide and boric acid, is a white powder soluble in dilute acids.

Scandium aurichloride, $3ScCl_3,2AuCl_3,21H_2O$, occurs in yellow, needle-shaped crystals, which are very deliquescent. After prolonged drying in a desiccator over sulphuric acid, an octahydrate is obtained, which changes to the dihydrate on heating for some time at 100°, and to the anhydrous salt on prolonged heating at the same temperature. The *platinocyanide*, $Sc_2[Pt(CN)_4]_3,21H_2O$, occurs in monoclinic prisms, crimson by transmitted and green by reflected light; it is soluble in water, forming a colourless solution, and practically insoluble in alcohol. Several lower hydrates appear to exist; the completely dehydrated salt is colourless.

Scandium chloroacetate, $(CH_2Cl\cdot CO_2)_2Sc\cdot OH,2H_2O$, occurs in stellate crystals; the *lactate*, $Sc(C_3H_5O_3)_3,6H_2O$, in white, feathery crystals, and the *malonate*, $C_3H_2O_4Sc\cdot OH$, sometimes as a crystalline powder and sometimes amorphous. According to the mode of preparation, the malonate contains 1 or $2H_2O$. A *basic malonate*, $C_3H_2O_4[Se(OH)_2]_2$, is obtained when scandium hydroxide is used in large excess. The *malate*, $C_4H_4O_5Sc\cdot OH,H_2O$, occurs in fine granules, which have a mousy odour; the *fumarate*, $C_4H_2O_4Sc\cdot OH,\frac{1}{2}H_2O$, occurs in microscopic crystals. The *tartrate*, $C_4H_4O_6Sc\cdot OH$, separates from a boiling solution in colourless crystals; the *racemate*, with $4H_2O$, comes down less readily on boiling than the tartrate; the l-*tartrate* has been obtained with 1 and $2H_2O$, and the *meso-tartrate*, with $1H_2O$, forms a white, granular precipitate.

Scandium αβ-dibromopropionate,

$$Sc(C_3H_3O_2Br_2)_3,Sc(C_3H_3O_2Br_2)_2\cdot OH,$$

is a white, amorphous powder. The *citrate*, $Sc_4(C_6H_4O_7)_3,6H_2O$, is much less soluble in hot than in cold water; a dihydrate and tetrahydrate have also been prepared. The o-*chlorobenzoate*,

$$C_7H_4O_2Cl\cdot ScO,Sc(C_7H_4O_2Cl)_2\cdot OH,$$

forms a white, amorphous precipitate; the m-*nitrobenzoate*,

$$Sc[C_6H_4(NO_2)CO_2]_3,4H_2O,$$

is a white, crystalline powder. The *phthalate*, $OH\cdot Sc{:}C_8H_4O_4,H_2O$, is a white, amorphous powder, and loses $\frac{1}{2}H_2O$ on heating at 110° for thirty-six hours. The *tetrachlorophthalate*, $OH\cdot Sc{:}C_8Cl_4O_4,6H_2O$, is also amorphous. *Scandium* 3-*nitro*-4-p-*toluidinobenzenesulphonate*,

$$[C_6H_4Me\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3]_2Sc\cdot OH,5H_2O,$$

occurs in feathery, scarlet crystals, which become anhydrous on heating

at 105°, the colour being then orange-yellow. *Scandium octamethyltetra-aminodihydroxy-*p*-dixanthylbenzenetetracarboxylate*,

$$C_{88}H_{79}O_{29}N_8Sc_5,$$

is a red powder.

The scandium used in preparing some of these salts was not spectroscopically pure; the chief object in using the slightly impure specimens being to find out whether a separation of the rare earths had been effected in preparing the salts. G. S.

Nitrides and Oxides from Aluminium Heated in Air. ÉMILE KOHN-ABREST (*Compt. rend.*, 1910, **150**, 1757. Compare Abstr., 1905, ii, 637; this vol., ii, 506).—A reply to Serpek (this vol., ii, 615). W. O. W.

Metal- and Metallic Oxide-Aluminas and their Use for Catalytic Reactions. M. KLEINSTÜCK (*Zeitsch. angew. Chem.*, 1910, **23**, 1105—1106).—When fibrous alumina (Abstr., 1908, ii, 261) is shaken up with ammoniacal solutions of the chlorides, nitrates, or acetates of various metals, or with colloidal solutions of other metals, adsorption takes place to a considerable extent. If the alumina is then well washed, dried on the water-bath, and finally gently ignited, a mass is left which possesses a characteristic colour depending on the metal used. The colours obtained with copper, iron, manganese, gold, palladium, platinum, chromium, cobalt, nickel, and silver, and with various combinations of these are described. Iron- and silver-alumina are both colourless; the former can be used as a delicate test for tannin, and the latter gradually becomes dark violet on exposure to light in the presence of air.

These metal-aluminas may be used for various catalytic purposes; thus copper-alumina oxidises the vapours of methyl-alcohol to formaldehyde, or the hæmatoxylin of log-wood extract to hæmatein. An aqueous solution of an alkali hydrogen carbonate is reduced by palladium-alumina to formaldehyde and formic acid. Manganese- and platinum-alumina rapidly decompose an aqueous solution of hydrogen peroxide. T. S. P.

Electrical Properties of Aluminium-Silver Alloys. WITOLD BRONIEWSKI (*Compt. rend.*, 1910, **150**, 1754—1757. Compare Petrenko, Abstr., 1905, ii, 635).—Determinations have been made of the electrical conductivity, temperature-coefficient of resistance between 0° and 100°, thermo-electric power at 0°, variation in thermo-electric power with temperature, and solution potential of a series of aluminium-silver alloys. The results are given in the form of curves, and these are shown to indicate the existence of only two definite compounds, Al_2Ag_3 and $AlAg_3$. Petrenko's compound, $AlAg_2$, and Pushin's alloy, AlAg, do not appear to be homogeneous substances. W. O. W.

Oxidation of Aluminium Amalgam. P. ROGER JOURDAIN (*Compt. rend.*, 1910, **150**, 1602—1604. Compare this vol., ii, 297).—The following observations appear to point to the existence of a carbonate and peroxide in the substance obtained by exposing aluminium

amalgam to air. On heating one gram of the product in a vacuum, 30 c.c. of a mixture of carbon dioxide and oxygen were obtained, the amount of the former depending on the proportion of the gas in the atmosphere to which the amalgam had been exposed. No oxidation took place in absence of moisture, but in presence of water vapour, direct absorption of oxygen occurred. The substance dissolved in acids with effervescence, carbon dioxide being liberated and hydrogen peroxide formed. W. O. W.

Alloys of Cobalt and Silver. F. DUCELLIEZ (*Bull. Soc. chim.*, 1910, [iv], 7, 506—507).—The alloys were prepared by heating together mixtures of silver and cobalt powders. The properties of the products obtained indicated that they were simple mixtures of the two metals.

The mixtures fused at about the melting point of cobalt, indicating insolubility of silver in cobalt. The silver tended to separate in a pure state; thus a mixture containing 95% of the metal furnished pure silver and an ingot containing 80·77% of this metal. All the alloys were attacked by hydrochloric acid; those rich in cobalt leaving silver powder, those moderately rich in cobalt giving lamellæ of silver, whilst those poor in cobalt retained their shape, but became brittle, and after treatment with the acid could be broken up by a hammer. On liquation, at a temperature intermediate between the melting points of the two metals, of an ingot containing 70·25% of silver, a drop of pure silver was obtained, and the lower part of the ingot became richer in silver. All the alloys were magnetic. After treatment with hydrochloric acid the surfaces of the alloys examined under the microscope showed (1) grey zones, often elongated, especially in those rich in cobalt, and (2) brilliant zones corresponding with silver. No eutectic product was observed. In a normal solution of cobalt sulphate the alloys furnished no *E.M.F.* with cobalt poles, but gave a constant *E.M.F.* of 0·535 volt with silver poles. T. A. H.

Alloys of Nickel and Silver. ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1910, [iv], 7, 621—622).—Alloys poor in silver are magnetic, slightly malleable, apparently homogeneous to the naked eye, but spongy and clearly heterogeneous when examined microscopically. When 50% or more silver is present, particles of this metal become visible to the naked eye. An alloy containing 70% of silver on re-melting separates into pure silver and nickel, containing 1·6% of silver. The alloys are attacked by hydrochloric acid, the nickel being dissolved, and silver left as a residue. With nickel poles in a normal solution of silver sulphate an *E.M.F.* varying from $-0·0021$ to $+0·0168$ volt is developed, and with silver poles an *E.M.F.* ranging from $-0·3962$ to $-0·4382$ volt, under otherwise similar conditions, indicating that the alloys are merely mixtures of the two metals (compare Ducelliez, preceding abstract). There is evidence of the formation of a weak solid solution of silver in nickel. T. A. H.

Solutions of Blue Molybdenum Oxide. A. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 20—21).—When molybdenum trioxide, suspended in water, is heated on the water-bath with a large excess of

powdered metallic molybdenum, a solution of the oxide Mo_3O_8 is obtained, which, according to cryoscopic measurements, contains unpolymerised molecules of the oxide. On addition of ammonium chloride, barium chloride, and other salts to this solution, polymerisation takes place, and the oxide passes into the colloidal form.

H. M. D.

Extraction of Germanium from Blendes. GEORGES URBAIN, M. BLONDEL, and OBIEDOFF (*Compt. rend.*, 1910, **150**, 1758—1760. Compare Abstr., 1909, ii, 1026).—Experimental details are given for extracting germanium from blendes containing traces of this element. After isolating a mixture of the sulphides of arsenic, molybdenum, and germanium, this is dissolved in the minimum amount of ammonia and the solution fractionally precipitated by acid of diminishing concentration. The whole of the arsenic and molybdenum is thus precipitated, leaving germanium in solution. Five grams of pure germanium have been obtained from 550 kilograms of a Mexican blende.

W. O. W.

Theory of the Preparation of Thorium Salts. I. Purification by means of the Sulphate. IWAN KOPPEL and H. HOLTKAMP (*Zeitsch. anorg. Chem.*, 1910, **67**, 266—292).—In the purification of thorium salts, the anhydrous sulphate is dissolved in water, yielding a highly supersaturated solution, from which a hydrate separates spontaneously. It has been shown by Roozeboom (Abstr., 1890, 686) that the octa-hydrate is at all temperatures labile with respect to the nona-hydrate, but the two solubility curves are very close to one another, and in practice the octa-hydrate is always obtained. In the technical method, the hydrated sulphate is precipitated by adding sulphuric acid to a concentrated solution of the chloride. The conditions of precipitation have now been investigated.

The formation of the tetra-hydrate must be avoided, on account of its bad filtering qualities, and of its considerable solubility in water at the ordinary temperature.

The solubility of thorium sulphate octa-hydrate in dilute sulphuric acid of different concentrations has been studied at 20°, 30°, and the boiling point. In each case the solubility falls with the concentration of the acid until 0·5% H_2SO_4 is reached, then rises to a maximum near 4% H_2SO_4, and again falls. When 33% H_2SO_4 is reached, the solid phase is converted into the tetra-hydrate at 30°, beyond which concentration the solubility is very small, and acid salts are formed. The solubility of thorium sulphate in nitric and hydrochloric acids at 30° shows maxima at 17% HNO_3 and 4·5% HCl respectively; minima are not observed. The presence of phosphoric acid in a solution in hydrochloric or nitric acid retards the precipitation of the sulphate, and also increases the solubility, so that when the quantity of phosphoric acid reaches 0·73 mol. P_2O_5 to 1 mol. ThO_2, sulphate is not precipitated. The crystallisation of the sulphate is slow, being incomplete after twenty-five hours. Raoult's law is found to be applicable to the vapour pressures of the hydrates and their solutions.

Hydrochloric acid is to be preferred to nitric acid for dissolving the

thorium before precipitation. The presence of an excess of solvent acid is without influence. The quantity of sulphuric acid should be 0 5% in excess of that theoretically required, and, in order to prevent the formation of the tetra-hydrate, the temperature must be below 42°, and preferably much lower.

The density and refractive index of solutions of pure thorium nitrate have been determined and tabulated. C. H. D.

Double Sulphates of Thorium. BARRE (*Compt. rend.*, 1910, **150**, 1599—1602).—The solubility curve for thorium sulphate in solutions of potassium sulphate of different concentrations at 16° shows branches corresponding with the following double salts, each of which has been isolated and analysed: $Th(SO_4)_2,K_2SO_4,4H_2O$, slender, interlacing needles; $Th(SO_4)_2,2K_2SO_4,2H_2O$, triclinic crystals (compare Berzelius, *Ann. Chim. Phys.*, 1830, [ii], **43**, 5); $Th(SO_4)_2,3{\cdot}5K_2SO_4$, small, triclinic crystals. The curve for thorium sulphate in solutions of sodium sulphate shows a maximum corresponding with the concentration 2·98% of Na_2SO_4; the only compound isolated was Cleve's salt, $Na_2Th(SO_4)_2,6H_2O$. The curve for solutions in ammonium sulphate shows three branches, agreeing with the existence of the double salt,

$$Th(SO_4)_2,3(NH_4)_2SO_4,3H_2O,$$

large, monoclinic prisms, and of the salts, $(NH_4)_4Th(SO_4)_4,2H_2O$ and $(NH_4)_2Th(SO_4)_3,4H_2O$, described by Rosenheim, Samter, and Davidsohn (Abstr., 1903, ii, 601). W. O. W.

Decomposition of Thorium Sulphate by Water. BARRE (*Compt. rend.*, 1910, **151**, 70—72).—Demarçay (Abstr., 1883, 1053) obtained a basic salt by the action of water on thorium sulphate, to which he attributed the composition $Th_4(SO_4)_7O,8H_2O$. This substance, however, appears to be a mixture of thorium sulphate with a basic salt, $ThO(SO_4),2H_2O$. The latter has been obtained crystalline by allowing Demarçay's product to remain in contact with water for a long time; 100 parts of water at 100° dissolve 0·023 part of the salt.

W. O. W.

The Atomic Weight of Vanadium. II. The Chlorine Content of Vanadium Oxytrichloride and the Ratio $V_2O_5:V_2O_3$. WILHELM PRANDTL and BENNO BLEYER (*Zeitsch. anorg. Chem.*, 1910, **67**, 257—266. Compare this vol., ii, 134).—A further series of four estimations of chlorine in vanadium oxytrichloride, four others being rejected, gave a mean value of 61·3348 ± 0·0087% Cl, or 51·061 ± 0·024 for the atomic weight of vanadium.

Vanadium pentoxide was prepared by distilling vanadium oxytrichloride into pure water, evaporating the solution, and gently heating the moistened residue until free from hydrogen chloride. The residue was then repeatedly moistened with nitric acid and heated to just below the melting point, finally fusing in a platinum boat in a stream of oxygen, yielding very long, glistening, brownish-red crystals, D_4^{18} 3·357.

The reduction by hydrogen took place in a large platinum boat in a Jena glass tube, the temperature being kept low at first and gradually

raised, so as to avoid fusion, yielding a black powder of vanadium trioxide, D_4^{18} 4·870. Owing to the very rapid oxidation of the trioxide, it was necessary to transfer the boat to a weighing tube in an atmosphere of hydrogen. Even in this way an entirely constant weight could not be attained. As a control, the trioxide was heated in oxygen until constant in weight. The atomic weight thus obtained for vanadium, $51·374 \pm 0·033$, may be too high, owing to the presence of a higher oxide than the pentoxide, and is in any case uncertain.

C. H. D.

Behaviour of Platinum and Nickel Wires to Hydrogen at High Temperatures. Marcello von Pirani and Alfred R. Meyer (*Zeitsch. Elektrochem.*, 1910, **16**, 444—447).—The resistance of a nickel wire increases when it is heated to a high temperature in a current of hydrogen; in the case of platinum the melting point is depressed by 250° to 300°, and the metal becomes brittle.

It is shown that the effect is not due to occlusion of hydrogen; it is not due to diffusion of furnace gases through the quartz tube used (if nitrogen is used instead of hydrogen it is not observed), and, further, the changes do not take place in a limited quantity of hydrogen. It is thought that the changes are probably due to the presence in the hydrogen of a small quantity of an impurity containing carbon, from which the metals take up carbon at or near their melting points.

T. E.

Mineralogical Chemistry.

Vanadium Deposits in Peru. D. FOSTER HEWETT (*Trans. Amer. Inst. Mining Engineers*, 1910, 40, (1909), 274—299).—The modes of occurrence and characters of deposits of vanadium ores at two distinct localities in Peru are described. In the Yauli district in province Tarma, a black, lustrous asphaltite occurs as a large, lenticular mass in sedimentary rocks of Mesozoic age. This has been previously described by Torrico y Meca as a vanadiferous coal (Abstr., 1896, ii, 276). As shown by a large series of analyses, the material varies widely in composition: moisture, 0·08—7·83; volatile matter, 8·26—49·02; free carbon, 31·15—90·58; S, 1·87—44·59; ash, 0·64—17·80; V_2O_5, trace—1·43% (V_2O_5 in ash, 2·3—64·3%).

In the Quisque (or Minasragra) district in province Pasco (Abstr., 1907, ii, 788) the vanadiferous minerals form a thick, lenticular vein in red shales of Cretaceous age, and are associated with dykes of igneous rocks. The central portion of the vein is composed of patronite (D 2·65—2·71, H 2½), the outer portions of quisqueite (D 1·75, H 2½), while between the two are bands of a coke-like material (D 2·4, H 4½). Analyses of purer patronite than that examined by W. F. Hillebrand gave 19·3—24·8% vanadium; the formula $V_2S_5 + nS$ is suggested.

By the oxidation of these ores, several secondary vanadium minerals are formed in abundance, and the mine-waters contain vanadium in solution. Preliminary descriptions, with partial analyses by W. F. Hillebrand, are given of red, brown, and green hydrated vanadium oxides and of a hydrated calcium vanadate. Some of these appear to represent new species (compare Nenadkevitsch, Abstr., 1909, ii, 411).

L. J. S.

Mineralogical Constitution of French Phosphorites. ALFRED LACROIX (*Compt. rend.*, 1910, **150**, 1213—1217).—Carnot has shown that many French phosphorites supposed to be fibrous forms of apatite are deficient or lacking in fluorine. Microscopical examination reveals three types: (1) a holocrystalline variety which is always fibrous; (2) an isotropic variety in thin, colourless or yellow, homogeneous sheets; (3) a mixture of crystalline and isotropic matter.

Analyses of the best samples of (2) and (3) showed that they were very similar, consisting mainly of calcium phosphate and calcium carbonate with a little fluoride. The microscopical and chemical properties agree with the assumption that the mixtures are closely related to dahllite [$Ca_6(PO_4)_4,CaCO_3,\frac{1}{2}H_2O$], and francolite

[$Ca_8(PO_4)_6(CaF)_2,CaCO_3,H_2O$].

It is suggested that Damour's hydroapatite is also a variety of francolite, the carbonic acid having been overlooked by Damour.

Colophanite from the Guano deposits in the Island of Sombrero is practically identical with the isotropic phosphate in the French deposits.

A new nomenclature is suggested for the phosphorites. Isotropic compounds of phosphate and carbonate are classed as *colophanites*, and mixtures of colophanite with optically negative, crystalline matter of similar composition are termed *quercyite*. A rarer form has been noticed in samples from Sombrero and Badajos, but seldom in French samples, in which both positively and negatively birefringent crystals are mixed with the colophanite. This is termed *β-quercyite*.

R. J. C.

[Identity of Pastreite with] Jarosite. AZÉMA (*Bull. Soc. franç. Min.*, 1910, **33**, 130—132).—The following new analyses of pastreite (Norman, 1866) from Saint-Félix-de-Pallières, dep. Gard, shows the presence of alkalis, and proves the identity of the mineral with jarosite $K_2O,3Fe_2O_3,4SO_3,6H_2O$ or $K_2[Fe(OH)_2]_6(SO_4)_4$. The mineral forms ochre-yellow, compact masses with a conchoidal fracture, and under the microscope it is seen to consist of minute crystals with strong negative birefringence. When heated to redness, it turns brown and gives off sulphur trioxide. It owes its origin to the action of the products of oxidation of iron-pyrites on the gangue:

SO_3.	Fe_2O_3.	K_2O.	Na_2O.	H_2O.	Insol.	Total.	Sp. gr.
32·02	48·63	7·75	0·55	10·61	0·29	99·85	3·02

L. J. S.

Silicate Fusions with Artificial Mixtures. VERA HAEMMERLE (*Jahrb. Min.*, 1910, *Beil.-Bd.*, **29**, 719—738).—In many of the previous experiments made with silicate fusions, the materials employed consisted of natural minerals; these are, however, never quite pure, and any unfused particles may exert an influence on the crystallisation of the mass. In the present experiments, pure chemicals (silica, magnesia, calcium carbonate, sodium carbonate, and aluminium hydroxide) were fused together in the proportions required by olivine, diopside, and labradorite, either alone or in the presence of natural magnetite. Mixtures of these materials corresponding with labradorite (20—80% in different fusions) and diopside (80—20%), together with 10% magnetite, resulted in the formation of the following minerals, which were determined under the microscope in thin sections of the product: diopside, soda-augite, alumina-iron-augite, hedenbergite, labradorite, anorthite, magnetite, spinel, and hæmatite; and mixtures corresponding to olivine, labradorite, and diopside, in various proportions, gave olivine, diopside, alumina-augite, labradorite, and nepheline. These results, which agree with those obtained when natural minerals supplied the materials fused together, point to various chemical reactions in the dissociated fused solutions. L. J. S.

Hornblende and Augite from the Rhön Basalts. XENIA GALKIN (*Jahrb. Min.*, 1910, *Beil.-Bd.*, **29**, 681—718).—The basaltic rocks, tuffs, and agglomerates of the Rhön Mountains contain large, well-developed crystals of hornblende and augite, which become isolated on the weathering of the rocks. Both minerals often occur together in the same rock. Seven analyses were made of hornblende crystals from different localities; these vary only slightly amongst themselves, and the mean is given under I. Under II is the mean of five analyses of augite from various localities:

	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
I.	40·65	3·76	0·88	13·87	8·36	4·57	12·34	12·23	2·27	1·14	0·45	100·52
II.	47·56	1·54	0·48	5·28	6·94	3·05	11·76	22·14	1·09	0·38	0·22	100·44

These analyses, together with others, are discussed at length in connexion with the formulæ proposed by Tschermak, Scharizer, Rosenbusch, and Penfield, but no definite conclusions are clearly stated. L. J. S.

Anophorite, a New Hornblende from the Katzenbuckel. WILHELM FREUDENBERG (*Mitt. Badischen Geol. Landesanstalt*, 1908, **6**, 45—84).—A detailed description is given of a variety of alkali-hornblende occurring as needles in basic streaks in the shonkinite rock of the Katzenbuckel in Baden. The pleochroism, $\mathfrak{c}$ (deep reddish-brown) $>\mathfrak{b}$ (green to yellowish-green) $>\mathfrak{a}$ (straw-yellow), resembles that of catophorite, but there are differences in optical orientation; in anophorite the plane of the optic axes is perpendicular to the plane of symmetry, and the angle of extinction, $\mathfrak{b}:c=20—28°$, is less than in catophorite. The etched figures are described in detail.

The following analysis, by O. N. Heidenreich, also shows differences

in composition, there being much less iron and more magnesium than in catophorite.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	SrO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
49·79	5·37	1·98	7·54	9·18	0·36	11·59	3·16	trace	1·85	7·92	1·52	100·26	3·166

L. J. S.

Chemistry of Submarine Glauconite. WILLIAM A. CASPARI (*Proc. Roc. Soc. Edin.*, 1910, **30**, 364—373).—Glauconitic greensand when digested first with hydrochloric acid and then with sodium hydroxide solution and shaken with boiling water yields a colloidal suspension of disintegrated glauconite; this, on addition of a trace of acid, gives a green, flocculent precipitate. Material containing varying amounts of calcium carbonate (5—33%) and quartz and other mineral grains (3—47%) was so treated, and the separated glauconite analysed, with the following results: (I) of material dredged from the Pacific off Panama at a depth of 556 fathoms, and (II) from the Agulhas Bank at 110 fathoms:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Loss on ignition.	Total.
I.	49·12	7·09	25·95	0·89	3·10	7·02	7·12	100·29
II.	51·15	7·61	18·83	2·79	4·54	7·80	7·56	100·27
III.	56·80	—	28·16	4·16	—	7·27	4·19	100·58

Including aluminium with ferric iron, and calcium, magnesium, and ferrous iron with potassium, these analyses agree fairly well with the formula $KFeSi_2O_6,H_2O$ (compare Collet and Lee, Abstr., 1906, ii, 370).

Under the microscope, grains of glauconite show a yellowish-green, birefringent material enclosed in a black, isotropic network of organic matter. The latter, when dissolved out by sodium hydroxide solution, gave C 54·85%, H 5·79%; it resembles humic acid. Glauconite possesses the property of absorbing dyes, as do clays and zeolites; and it also absorbs water from a moist atmosphere, being capable of holding up to 30·35% H_2O. It is therefore suggested that glauconite is a colloidal silicate, the pleochroism and optical birefringence being probably the result of strain set up by the network of organic matter.

An artificial product resembling glauconite was obtained by mixing colloidal solutions of a complex ferric radicle (potassio-ferric tartrate) and potassium silicate; the clear, greenish-blue jelly so formed was heated under pressure at 180° for some hours, when grass-green, flocculent particles separated; this gave analysis III above. The presence of an organic acid (no doubt humic acid in nature) appears to be essential for the formation of glauconite. L. J. S.

The Fireclay [and Sideroplesite] of Glenboig, Lanarkshire. JOHN WALTER GREGORY (*Proc. Roy. Soc. Edin.*, 1910, **30**, 348—360).—The Glenboig fireclay forms a bed, six feet in thickness, in the shales and sandstones of the millstone-grit series. Unlike the fireclays of the coal-measures, it is not overlain by a bed of coal, neither does it contain any fossil roots of plants. The fine-grained clay-substance forming the bulk of the material is present as minute, rounded granules, about

0·001 mm. diameter; it is amorphous, and not crystalline, and is referable to halloysite rather than to kaolinite (see following abstract). Embedded in it are abundant grains of quartz, some grains of felspar, and minute, lenticular, zonèd crystals of a rhombohedral carbonate. Analysis, by D. P. McDonald, of the last shows it to be the sideroplesite variety of chalybite, with $FeCO_3$ 88·4, $MgCO_3$ 8·3, $CaCO_3$, 3·3%:

CO_2.	CaO.	MgO.	FeO.	Fe_2O_3.	H_2O.	Insol.	Total.	Sp. gr.
33·26	1·56	3·39	46·45	6·49	[0·79]	8·06	100·00	3·63

L. J. S.

Nature of the Clay-substance of Fireclay of Glenboig, Lanarkshire. DAVID P. McDONALD (*Proc. Roy. Soc. Edin.*, 1910, **30**, 374—377. See preceding abstract).—The finest material separated by repeated washing from the fireclay was dried in a steam-oven and analysed with the following results. The dried material had a decided buff colour, and under the microscope some free quartz was detected:

SiO_2.	$Al_2O_3(+Fe_2O_3)$.	CaO.	MgO.	H_2O at 105°.	H_2O combined.	Total.
46·67	37·65	0·16	n. d.	2·13	12·66	99·27

This analysis points to either kaolinite or halloysite, although the water percentage is slightly higher than that (14·0) required by the kaolinite formula $2H_2O,Al_2O_3,2SiO_2$. The facts that the material is amorphous and is decomposed by acid suggest, however, that it is halloysite rather than kaolinite. When the washed clay is boiled with strong hydrochloric acid for two hours, 6·5% Al_2O_3 goes into solution, and after thirteen hours 36·6% Al_2O_3 is dissolved. Halloysite from Dordogne yielded 2·2% Al_2O_3, and lenzinite from the Eifel 21·97%, after two hours' boiling with hydrochloric acid. L. J. S.

Study of Laterites. H. ARSANDAUX (*Compt. rend.*, 1910, **150**, 1698—1701).—The laterites examined are supposed to be normal muscovites in which water of constitution has progressively replaced the alkalis. Analysis of a series of more or less exposed samples from the same bed confirms this view.

A progressive secondary change gradually replaces the silicates with hydrated oxides of iron and aluminium, the proportion of the latter being greater the nearer the micaceous products are to kaolinite. Part of the hydrated alumina appears to be formed directly from the muscovite, and part passes through the intermediate stage of kaolinite.

R. J. C.

The Amount of Thorium in Sedimentary Rocks. I. Calcareous and Dolomitic Rocks. JOHN JOLY (*Phil. Mag.*, 1910, [vi], **20**, 125—128).—Thirty-four rocks, mainly limestone, chalk, dolomite, marble, and oolite, were examined for thorium by methods previously employed, but detectable quantities were found only in six specimens, the maximum quantity being only $0·22 \times 10^{-5}$ gram of thorium per gram. The amount detectable was from 0·03 to 0·06, according to the quantity of material dealt with. It would appear

from these results that thorium, of which $0 \cdot 9 \times 10^{-8}$ gram has been found per gram of sea-water from the Indian Ocean, is selectively rejected in the organic processes attending the abstraction of the lime.

F. S.

Physiological Chemistry.

The Fundamental Bodily Needs of the Infant, as Determined by Measurement of the Gaseous Exchange. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1910, 26, 14—40).—The gaseous exchange in various infants during a period of fasting, and when at complete rest, was determined. Under these conditions it was found that the infant produced, on an average, 12 grams of carbon dioxide per square metre of body surface, and consumed 11 grams of oxygen. The nitrogen excreted was also estimated, and from the numbers obtained, the amount of fat and carbohydrate consumed was estimated. It was found that a child of 4325 grams weight consumed 273 calories in twenty-four hours when kept at a temperature of 20°. S. B. S.

Influence of Oxygen Inhalations on Muscular Work. LEONARD E. HILL and MARTIN FLACK (*J. Physiol.*, 1910, 40, 347—372). —A full account of researches of which several preliminary communications have already been published. They support the authors' contention that inhalation of oxygen is beneficial to athletic work. W. D. H.

Action of Certain Substances on the Respiratory Centre. ARTHUR S. LOEVENHART and W. E. GROVE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xvi—xvii).—Sodium iodosobenzoate cannot oxidise phenolphthalin to phenolphthalein, but it can do so in the presence of serum. The oxygen united to the iodine in iodosobenzoic acid is, therefore, capable of physiological utilisation. This is supported by the effects of iodoxybenzoate or iodosohydroxybenzoate when injected intravenously in animals; the respiratory centre is very sensitive to changes in oxidative processes, and it is immediately and markedly depressed. This leads to apnœa, recovery from which is spontaneous. The taste of sodium iodosobenzoate is further indistinguishable from that of hydrogen peroxide, and is probably in both cases due to the action of active oxygen on the end-organs of taste. W. D. H.

The Estimation of the Quantity of Blood by means of the "Optical Method." EMIL ABDERHALDEN and JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, 66, 120—127).—The principle of the method consists in estimating the change in the rotation of the plasma produced

by injecting an optically active substance. Substances suitable for this purpose must have a high rotatory power, be easily soluble in isotonic saline, in which solution they should not cause marked change in the isotony of the blood, and should be non-toxic. Dextrin fulfils these conditions, and by the method it was calculated that the amount of blood in different dogs varied between 11·3 and 12·4% of the total body-weight. The blood should be withdrawn at as short an interval as possible after the injection of the dextrin. S. B. S.

The Action of Pure Choline on Blood Pressure. EMIL ABDERHALDEN and FRANZ MULLER (*Med. Klinik.*, 1910, No. 22. Compare this vol., ii, 530).—Further data are given which support the authors' statement that the typical effect choline produces on arterial blood pressure is a lowering. This is partly due to action on the heart, but mainly to dilatation of peripheral vessels. The drug, however, is believed to act on both varieties of vaso-motor nerves, and it is not until the vaso-dilators are paralysed by atropine that the effect on the vaso-constrictors is seen. W. D. H.

Vasotonin, a New Drug which Lowers Blood Pressure. FRANZ MÜLLER and BRUNO FELLNER (*Therapeut. Monatsheft*, 1910, **24**, June).—The name vasotonin is given to a combination of yohimbine and urethane, which produces a fall of blood pressure due to vaso-dilatation, and appears to have considerable therapeutic value. W. D. H.

Peritoneal Blood Transfusion. ARTHUR E. BOYCOTT (*J. Path. Bact.*, 1910, **14**, 605—614).—Blood transfused into the peritoneal cavity and subsequently absorbed into the circulation is destroyed more quickly than blood transfused directly into the veins. This may be due to the red cells being rendered relatively more foreign by their passage through an extravascular position. The mechanism of destruction is the same, except that plagocytosis of red cells in the lymph glands and spleen is more prominent. W. D. H.

Anticoagulants and Frog's Blood. HAROLD PRINGLE and JOHN TAIT (*Proc. physiol. Soc.*, 1910, xxxv—xxxvi; *J. Physiol.*, **40**).—In Amphibia as in Crustacea, blood coagulation consists of two events: the first, connected with the coagulation, caused by thrombocytes or explosive cells, and the second, a general jellying of the plasma. Snake venom, peptone, and novocaine prevent both occurrences. In the case of the two first-named anticoagulants, the amœboid movements of the leucocytes are marked; with novocaine they are slight or absent. In coagulation *in situ* at a wound in a tadpole's tail, both agglutination of thrombocytes and a localised coagulation may be observed. W. D. H.

Blood Coagulation in the Amphipod, Gammarus. JOHN TAIT (*Proc. physiol. Soc.*, 1910, xli; *J. Physiol*, **40**).—The local stoppage of a wound in *Gammarus* is due to cell agglutination, and this is the only visible factor in specimens from the upper tide limit.

In *Gammarus locusta* found lower in the ebb, globule formation associated with explosion of thrombocytes is the prominent feature.
W. D. H.

The Reaction of Blood to Silver Hydrosol. GIOACCHINO BRECCIA (*Zentr. Physiol*, 1910, **24**, 253—258).—The precipitating substance in the blood is thermostable, and occurs in the red corpuscles; the action varies with the amount of hæmoglobin, but the thermostability is against the material being hæmoglobin. W. D. H.

The Composition and Properties of White-Blood Corpuscles. STEFANO MANCINI (*Biochem. Zeitsch.*, 1910, **26**, 140—148).—The leucocytes were obtained by allowing large quantities of oxalated horse blood to remain in tall cylinders, mechanically separating the layer of white corpuscles thus formed, and then washing them repeatedly with physiological saline containing a little toluene and minute quantities of ammonium oxalate, which substance inhibits clotting. From 30 litres of blood, 30 c.c. of moist leucocytes could be obtained, which contained appreciable quantities of calcium oxalate. The leucocytes were, with exception of a small residue, soluble in 0·1% sodium carbonate, from which solution a precipitate was formed on addition of acetic acid. The chief constituent of this precipitate appeared to be a nucleoprotein. The leucocytes, on treatment with acid, yielded a trypsin-like ferment, which could digest fibrin in presence of alkali. Pepsin was not found. Diastase was present, but not lipases. The leucocyte extract exerted a rennet-like action, and also clotted goose-plasma; a laccase could also be detected, but not a glycolytic ferment. The leucocytes exerted an antihæmolytic action on saponin and tetanus toxin, although no antitetanic action could be detected in experiments on animals. S. B. S.

The Biology of the Phagocytes. VII. The Influence of Calcium Ions on Chemiotaxis. HARTOG J. HAMBURGER (*Biochem. Zeitsch.*, 1910, **26**, 66—84).—It was shown by the two following methods that calcium ions promote chemiotaxis: (*a*) Capillary tubes with calcium-free and calcium-containing cultures were introduced under the skin of rabbits, and the length of the column of leucocytes entering the tubes was measured; (*b*) calcium-containing and calcium-free saline were introduced into the rectum of different rabbits, and then the length of the leucocyte column was measured which was formed when capillary tubes of bacterial cultures were introduced under the skin. Experiments were also carried out in a similar way with filtrates from bacterial cultures. In all cases, calcium salts stimulated the activity of the phagocytes. Calcium-containing natural mineral waters also stimulate phagocytes. S. B. S.

Hæmolysis by Lipoids. H. LIEFMANN and MICHAEL COHN (*Biochem. Zeitsch.*, 1910, **26**, 85—115).—Hæmolysis by lecithin or oleic acid is not appreciably affected by the addition of immune amboceptors (rabbit immunised against sheep's blood) when the latter is added in weak concentration; hæmolysis by soaps, on the other hand,

is delayed. Probably the inhibition by protein plays a *rôle* as well as the specific amboceptor action. Hæmolysis by lecithin is inhibited by small amounts of cholesterol; hæmolysis by oleic acid and soaps, on the other hand, is only slightly inhibited by relatively large quantities of this substance. The "albumin" fraction of guinea pigs serum ("end piece" of the complement) binds soap, lecithin, and oleic acid, whereas the "globulin" fraction ("middle piece") binds soaps strongly, lecithin not appreciably, and oleic acid not at all. Furthermore, in cases of immediate total hæmolysis by addition of hæmolytic lipoids, and subsequent addition of serum, the latter can be replaced by "albumin," but not by "globulin." In the case of hæmolysis by commercial lecithin preparations, it is not only the impurities, but the lecithin itself, which plays a part. S. B. S.

The Residual Carbon of the Blood. STEFANO MANCINI (*Biochem. Zeitsch.*, 1910, **26**, 149—156).—By "residual carbon" is meant that amount of carbon which remains in the blood after precipitation of the protein contents by phosphotungstic acid. It was determined by Messinger's method of oxidation by acid dichromate mixture. The amount found in blood of the same species was approximately constant (mean 0·780 gram in 100 c.c. of blood). No great deviations were observed, however, in blood of different species of animals (variations from 0·0756 to 0·0844 gram per 100 c.c. blood). By keeping the blood cool for twenty-four hours, no marked changes in this amount were observed. About half the residual carbon is in the form of sugar (analysis by Pflüger's method). The quantity of residual carbon increases after loss of blood, and after ligature of the kidney vessels and ureters. It also increases after gradual phosphorus poisoning. S. B. S.

A New Form of Blood gas Pump. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1910, **40**, 373—377).—The apparatus described and figured is a modified Toepler pump. The main improvement is the entire absence of taps and joints, and, consequently, of leakage. W. D. H.

Lipase. HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, *J. Biol. Chem.*, 1910, **7**, xvii—xviii).—The amount of human pancreatic lipase determines the extent of digestion, that is, the point of final equilibrium between the triolein and the products of its hydrolysis. When lipase is abundant, digestion is practically complete; when triolein is relatively abundant, the percentage hydrolysis is small, although the actual amount of acid liberated may be considerable.
W. D. H.

The Nutritive Value of Some Soluble Pentosans, Mannans, Lævulans, and Galactans. MARY DAVIES SWARTZ (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xliv—xlv).—Galactans are not appreciably affected by any of the micro-organisms used; pentosans, mannans, and lævulans are gradually decomposed by soil and fæcal anaërobes. When introduced parenterally they are not

retained or altered by the organism, but are gradually excreted in the urine. Those hemicelluloses which are most readily attacked by bacteria disappear most completely from the alimentary tract (man or dog). There is no justification for considering these carbohydrates as of any appreciable nutritive value. W. D. H.

Gastric and Peptic Digestion of Fibrin. Variations of the Ratio Fibrin/Hydrochloric Acid Solution. EUGÈNE CHOAY (*J. Pharm. Chim.*, 1910, [vii], 1, 521—528).—In the previous paper (this vol., ii, 516) the variation of the ratio F/G or P, where F is dry pork fibrin, G a dry extract of the stomach membrane of the pig, and P commercial pepsin, was investigated under conditions in which the ratio of the fibrin to dilute hydrochloric acid (0·25%) remained constant. In the present paper the effects due to variation of the latter ratio are considered. The hydrochloric acid used was of 0·25% strength throughout the experiments, and two ratios F/HCl solution were investigated, namely, 2·5/60 and 2·5/120. The ratios F/G or P used were 6·25/1, 25/1, and 1000/1. The determinations made were those suggested previously. The results, which are tabulated in detail in the original, show that under these conditions dilution quickens the dissolving power of considerable quantities, but slows the activity of moderate and small quantities of the gastric ferments, and that under all conditions total gastric extract is more active than pepsin. T. A. H.

The Catabolism of Methylated Xanthines. JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, 67, 155—160).—The fate of methylated xanthines is of interest, as they occur in tea, coffee, and cocoa. Previous work has shown that 20—50% appear in the urine as monomethylxanthine, some leaves the body unchanged, and a part is oxidised to an unknown end product in which the purine ring is broken down. The question investigated in the present research is, in what organ does the change occur, and experiments were performed *in vitro* with minced organs and tissues. Blood, liver, kidney, spleen, lung, and muscle were used; all produce the effect to about the same degree. W. D. H.

Purine Metabolism in Hibernating Animals. ERNEST L. KENNAWAY (*Bio.-Chem. J.*, 1910, 5, 188—191).—Dormice, when awaking from hibernation, were found to contain 30% more purine nitrogen than was present before or during hibernation. The results indicate that a synthesis of purines takes place at the time of awakening. W. D. H.

Repeated Fasting. PAUL E. HOWE and PHILIP B. HAWK. **Fasting Studies on Men and Dogs.** P. E. HOWE, H. A. MATTILL, and P. B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xlvi, xlvii—xlviii).—A second fast, following a first of fifteen days, lasted twice as long. There was a more gradual loss of weight in the dogs, a much lower and more constant nitrogen output, a slight rise in ammonia, and a more gradual drop in

the creatine excreted, but this was followed in both fasts by a rise towards the end. The loss in body-weight was 45·8% in the first, and 46·8 in the second fast.

In the second paper further, experiments of the same kind are recorded, one dog fasting for one hundred and seventeen days, the longest on record; it was carefully fed back to health and started on a second fast. The men fasted seven days, and lost 7·7% of weight. Details are given of the composition of the urine, particular attention being paid to creatine and creatinine. W. D. H.

Occasional Occurrence of Urobilin in Gastric Juice. PIERRE LAVIALLE (*Chem. Zentr.*, 1910, 1, 1732; from *Bull. Sci. Pharmacol.*, 1910, **17**, 105—107).—In three cases urobilin was detected in the gastric juice of invalids, being formed, in the author's opinion, by bacterial reduction of the bile pigment which passed from the duodenum to the stomach. The gastric juice did not show Gmelin's reaction. E. J. R.

The Nitrogen Balance in Pregnant Dogs. JOHN R. MURLIN. **The Protein Metabolism of Parturient Women.** J. R. MURLIN and THORNE M. CARPENTER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, x, xlix).—The amount of nitrogen lost is not greater in the early weeks of gestation than it is in complete sexual rest. In the menstrual period, there is marked retention of nitrogen.

The urine in women during the last few weeks of pregnancy and the puerperium shows the usual parallelism between total nitrogen and sulphur. Just previous to parturition, there was in one case a rise in creatine excretion. The creatine is also high during the puerperium, whilst involution of the uterus is occurring. W. D. H.

Pentose in the Pancreas. WALTER A. JACOBS and PHŒBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, ix).—The only pentose occurring in the nucleo-proteins of the pancreas and liver is *d*-ribose. W. D. H.

Action of Bile and Bile Salts on the Tonus of Automatic Movements of the Intestine. G. D'ERRICO (*Zeitsch. Biol.*, 1910, **54**, 286—298).—Bile or bile salts added to Ringer's fluid lower the tonus of the intestine (large and small) of the cat, and its rhythmical movements are diminished. W. D. H.

Lipoids. XI. Comparative Chemistry of the Brain. SIGMUND FRÄNKEL and KURT LINNERT (*Biochem. Zeitsch.*, 1910, **26**, 44—52).—Brain substance from various animals, and from different parts of the human brain (cortex, medulla, medulla oblongata, cerebellum, etc.), was submitted to analysis by the following method: The brain, made into a paste, was either dried to constant weight or treated first with warm acetone and then with hot acetone, the extracts mixed, and the amount extracted and the residue weighed. By either

of these methods the amount of water could be ascertained. The dried substance was then extracted successively in a Soxhlet apparatus with hot acetone, low boiling petroleum, benzene, absolute alcohol, and 80% alcohol. The amount extracted by these solvents was thus estimated, and the results expressed in percentages of fresh brain, dried brain, and total lipoids. Considerable variations were found in the different samples analysed, and the authors give their results in tabular form.

S. B. S.

The Place of Formation of Uramic Acids. PETER PHILOSOPHOFF (*Biochem. Zeitsch.*, 1910, **26**, 131—139).—The investigations were undertaken with the object of throwing light on the mechanism of urea formation in the body, and of testing Hofmeister's hypothesis of the formation of this substance by the oxidative synthesis of ammonia with an amino-acid residue. When ox-blood containing taurine was perfused through ox-liver, no taurocarbamic acid could be detected; if, however, a mixture of taurine and glycine were added to the blood, the carbamic acid could be detected after perfusion. The acid was not in this case isolated in a crystalline form, but its presence was determined by the isolation of its acid products of hydrolysis. The author gives full experimental details as to the methods of isolation of taurocarbamic acids from animal fluids. S. B. S.

A Reducing Endo-enzyme in Liver and Kidney. DAVID FRASER HARRIS (*Bio-Chem. J.*, 1910, **5**, 143—160).—A full account of a research previously published (this vol., ii, 324). W. D. H.

Heat Production of Muscle. A. V. HILL (*J. Physiol.*, 1910, **40**, 389—403).—The heat production during the twitch of a frog's muscle lasts a very short time normally; if it lasts longer (several minutes), "contracture" is present. Normal saline solution increases the "tone," but if the amount of contraction is the same as in the absence of the increased tone, heat production is decreased. The view is advanced that the heart is analogous to a muscle stimulated at regular intervals; if this is so, the tonic condition of the heart involves far less energy breakdown than the condition in which the heart beats from complete diastole. W. D. H.

The Relationship between Muscular Rigor and Protein Coagulation; Chemical Stimulation of Muscle. I. ERNST ROSSI (*Zeitsch. Biol.*, 1910, **54**, 299—328).—After the action of ammonia gas, the frog's skeletal muscles lose the capacity to undergo rigor under the influence of chloroform and ether. Ammonia, however, has no influence if applied subsequent to the rigor produced by chloroform or ether. Certain differences in the action of ammonia are noted in relation to concentration and temperature. In the early stage of chloroform and ammonia rigor, the muscle recovers its irritability on withdrawal of the reagent. In later stages this is not so. In hypertonic sodium chloride solution the sensitiveness of muscle to chloroform and ammonia is increased; in isotonic sucrose solution it is lessened.

W. D. H.

Do Muscle and Blood-serum contain Creatinine? PHILIP A. SHAFFER and E. A. REINOSO (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem*, 1910, 7, xxx).—Fresh dog's muscle and dog's blood-serum contain respectively 1—6 mg. and 1 mg. of creatinine. The view that creatinine arises in muscle tissue is supported. W. D. H.

Phosphorus in Beef. C. K. FRANCIS and PERRY F. TROWBRIDGE (*J. Biol. Chem.*, 1910, 7, 481—501).—Any method which involves heating of the solution before precipitation of inorganic phosphorus gives incorrect results, as organic compounds are converted into inorganic by heat. From 52 to 65% of the total phosphorus in cold-water extracts of beef is in the organic form; this may be reduced to from 9 to 20% by heating to 70°. The round of beef contains more phosphorus soluble in cold water than any other cut. It is found chiefly in the muscular and connective tissues; the fat contains but little. The flesh of a thin animal contains more soluble phosphorus than that of a fat animal. W. D. H.

Purine Enzymes of Guinea Pig and Rabbit. PHILIP H. MITCHELL (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xi).—The purine enzymes in the two animals are the same; this suggests the possibility that the relationship of species may be indicated by the distribution of these enzymes. W. D. H.

Colour Change in the Isopod, Ligia oceanica. JOHN TAIT (*Proc. physiol. Soc.*, 1910, xl—xli; *J. Physiol.*, 40).—The colour changes in the surface of this animal are due to chromatophores, but their stimulation by light is indirect, the eye being the receptor organ. W. D. H.

Manganese in Fresh-water Mussels. HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxvi—xxxvii).—Manganese can be detected in most of the organs of the fresh-water mussel, and is most abundant in the gills and mantle. The eggs and embryo also contain it. The source of the element is the food of the animals, crenothrix and diatoms, which are able to concentrate manganese from its very dilute solution in the water. In lakes where the water is very pure, neither crenothrix nor mussels are found. The manganese probably has a respiratory function in the tissues and blood of these lamellibranchs. W. D. H.

The Behaviour of Nucleic Acid in the Cleavage of the Sea-urchin's Egg. ERNST MASING (*Zeitsch. physiol. Chem.*, 1910, 67, 161—173).—The nucleic acid in the fertilised egg of the sea-urchin does not increase as cell division goes on; although the mass of the nuclei may be increased a hundred fold, the amount of nucleic acid is hardly raised at all. Nucleic acid and the chromatin of histologists cannot, therefore, be identical. W. D. H.

Is Bence-Jones' Protein Produced from Osseo-albumoid? JACOB ROSENBLOOM (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, xiv—xvi).—Some of the results in the urine after admin-

istering digested osseo-albumoid either by the mouth or under the skin indicate that Bence-Jones' protein may be formed from osseo-albumoid by the action of enzymes in the bone marrow; but this view is put forward with considerable reserve. W. D. H.

The Presence of Insoluble Salts of Calcium (Oxalate and Phosphate) in Renal Calculi in Large Amount in a Preponderating Number of Cases, and the Bearing of this Finding on Calcium Metabolism in Gout and Allied Conditions. W. W. MACKARELL, BENJAMIN MOORE, and W. THELWALL THOMAS (*Bio.-Chem. J.*, 1910, **5**, 161—180).—Analyses of a number of renal calculi are given which bear out the statement contained in the title. There is no hope of dissolving such stones by lessening the alkalinity of the blood, for even when powdered they dissolve very slowly even in 1 in 4 hydrochloric acid. Anti-acid treatment, however, such as is employed in gout, would probably lead to more rapid growth of such calculi. W. D. H.

Elimination of Nitrogenous Waste during Renal Excretion in the Starving Subject. Relation of this Elimination to that of Water, the Vehicle for Urinary Excreta. Independence of the Two Phenomena. AUGUSTE CHAUVEAU and CH. CONTEJEAN (*Compt. rend.*, 1910, **150**, 1647—1652. Compare *ibid.*, 1478).—A series of experiments were carried out on dogs in a state of starvation. The urine was measured at regular intervals, and the total nitrogen estimated. At the commencement of the last period in each series, a considerable bulk of water was introduced into the system through the stomach or per rectum. No definite proportionality was observed between the volume of water eliminated and the amount of nitrogen. The authors consider that variations in the amount of urine excreted do not seriously affect the conclusions to be drawn from metabolism experiments. Even in experiments of short duration, the renal excretion of nitrogenous material remains a trustworthy index of the extent of protein degradation. W. O. W.

Glycuronic Acid and Ethereal Sulphates in Human Urine. CARL TOLLENS (*Zeitsch. physiol. Chem.*, 1910, **67**, 138—154).—A healthy man excretes as a rule twice as much glycuronic acid as ethereal sulphates (0·35 : 0·18 gram), but the former substance may rise considerably without being a pathological sign. Indole given by the mouth unites mainly with sulphuric acid, phenol with glycuronic acid. The two substances, as a rule, rise and fall together, usually but not always proportionally to the amount of intestinal putrefaction. In peritonitis and enteritis there is a marked increase in both. The same is true in cresol poisoning. W. D. H.

The Urine in Eclampsia. LYMAN B. STOOKEY (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, 1).—In eclamptic urine (five cases) the urea nitrogen is low; the ammonia nitrogen and mono-amino-acid nitrogen are both high. There was also a positive *p*-dimethylaminobenzaldehyde reaction. Washing out the colour with a

weak antiseptic solution and a low protein dietary lessened these peculiarities and also the clinical signs. In two cases a similar result followed the administration of iodides and thyroid. W. D. H.

On the So-called Thermo-soluble Protein of Bence-Jones. A CHRISTIAENS, AIME GÉRARD, and C. THOMAS (*J. Pharm. Chim*, 1910, [vii], **1**, 582—585).—The urine of a patient suffering from albuminuria was examined several times during some months. The urine constantly gave the Bence-Jones reaction, but the earlier specimens when half saturated with sodium chloride did not lose their thermo-solubility entirely, whilst in later specimens similar treatment caused the thermo-solubility to disappear completely. Dextrose, biliary pigments, and urobilin were absent. Under the microscope, numerous granular hyaline cylinders were observed as well as epithelial cells of renal origin. A litre of the urine contained 2·61 grams of serin and 0·08 gram of globulin. The results confirm Grimbert's opinion that the Bence-Jones reaction is not that of a specific protein, but is given by many of these substances (compare Abstr., 1908, ii, 212; Gascard and Devalmont, *ibid.*, ii, 519). T. A. H.

A Case of Alcaptonuria. A. RAVOLD and WILLIAM H. WARREN (*J. Biol. Chem.*, 1910, **7**, 465—480).—A case of this comparatively rare condition is described with full clinical details. The analysis of the urine, including the separation and identification of homogentisic acid, is also described in full. No new feature of importance appears to be noted. W. D. H.

The Behaviour of *p*-Aminophenylalanine in Alcaptonuria. LEON BLUM (*Zeitsch. physiol. Chem.*, 1910, **67**, 192—193).—Abderhalden and Massini (this vol., ii, 638) found that *p*-aminotyrosine increases the excretion of homogentisic acid in alcaptonuria, or rather that the reducing power of the urine is increased. In the present research, *p*-aminophenylalanine was given to one of these patients; there was a small rise in the homogentisic acid of the urine, but it is too small to indicate with certainty the transformation of one substance into the other. W. D. H.

The Amount of Cholesterol and Cholesterol Esters in the Normal and Atheromatous Aorta. ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1910, **67**, 174—176).—The amount of free cholesterol and still more so that of cholesterol esters is increased in atheromatous as compared with normal aorta.

The figures given are:

	Free cholesterol.	Cholesterol as ester.
1. Normal aorta	0·119%	0·047%
2. ,, ,, ...	0·103%	0·032%
3. Atheromatous aorta...	0·741%	1·053%
4. ,, ,, ...	0·673%	0·792%

W. D. H.

Lactic Acid in Diabetes. JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1910, li—lii; *J. Physiol.*, **40**).—One hundred to two hundred and fifty

c.c. of the urine are rendered slightly alkaline with sodium carbonate, evaporated, and extracted with alcohol. The extract is evaporated to a syrup, and strongly acidified with phosphoric acid. The ether soluble acids are then transferred to dilute sodium carbonate solution by shaking ether alternately with the syrup and sodium carbonate solution. This solution is then evaporated to dryness, and the lactic acid in it estimated by the author's distillation method. The normal excretion of lactic acid is less than 0·02 gram per diem. In diabetes it rises to 0·05—0·6. After an abundant meal of carbohydrates, the lactic acid rises to five times the normal amount. In both cases the lactic acid therefore probably originates from a partial conversion of the sugar of the blood into the acid. Lactates given by the mouth increase the lactic acid in the urine; the retention of, and presumably the ability to use, lactic acid is not much less in the diabetic than in the normal person. W. D. H.

Deterioration of Diphtheria Antitoxin. EDWIN J. BANZHAF (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xlv–xlvi).—The amount of deterioration was determined under various conditions; the deterioration of antitoxic citrated plasma was extremely low, even at room temperature. W. D. H.

Gastrotoxin and the Healing of Gastrotoxic Ulcers. CHARLES BOLTON (*J. Path. Bact.*, 1910, **14**, 418—431).—Gastrotoxic serum may be obtained by immunising animals (rabbits) with rabbits' gastric cells. The ulcers produced are due to self-digestion. They heal in a few weeks whatever the acidity of the juice may be. A sloughing ulcer lowers the acidity, but during healing the acidity is normal. Hyperacidity occasionally occurs.

If the stomach movements are normal, neither *Bacillus pyocyaneus* nor *B. coli communis* are able to delay the healing process. W. D. H.

Cell-Proliferation. CHARLES POWELL WHITE (*J. Path. Bact.*, 1910, **14**, 450—462).—Aseptic abscesses formed by the subcutaneous injection of turpentine or higher fatty acids become lined with squamous epithelium; the same is true for injections into the mammary gland, but an epithelial lining does not form unless the ulcers come into contact with epithelium. The endothelium in the neighbourbood also proliferates, and this is regarded as a phagocytic reaction. The experiments do not afford any evidence in favour of a direct formative irritant. W. D. H.

Physiological Action of the Sulphurous Acid Contained in White Wines. JEAN GAUTRELET (*Ann. Falsif.*, 1910, **3**, 226—235).—The results are recorded of a considerable number of experiments in which dogs and men received food and wine containing sulphurous acid; the administration of the latter was continuous for some length of time after the subjects had been kept under observation during a fore-period. The investigation was carried out by a Commission; the general conclusion, arrived at from a consideration of the effects

observed, is that sulphurous acid, in quantities up to 400 mg. per litre of wine, is not injurious to health, even when one-fourth of the quantity of acid just mentioned is present in the free state in the wine. W. P. S.

Anæsthetics. AUGUSTUS D. WALLER, F. W. HEWITT, and SIR FREDERICK TREVES (*Brit. Assoc. Report.*, 1909, 296—315).—The report deals with the Routine Use of a Mixture of Chloroform and Ether [with JOSEPH BLUMFELD], a description of the Chloroform Balance, the Physiological Effects of Mixed Anæsthetics, the Comparative Action on Isolated Muscle of Alcohol, Ether, and Chloroform, the Percentage of Chloroform in the Blood of Anæsthetised Animals and of Man under Various Conditions [with JOHN A. GARDNER and BUCKMASTER], and the Comparative Power of Chloroform, Ether, and Alcohol gauged by Intravenous Injection [with W. L. SYMES]. E. H.

Products of the Decomposition of Chloroform in the Organism. MAURICE NICLOUX (*Compt. rend.*, 1910, **150**, 1777—1778. Compare this vol., ii, 637).—Desgrez has signalised the decomposition of chloroform into carbon monoxide and water under the influence of aqueous alkalis (Abstr., 1898, i, 166 ; ii, 530). This decomposition proceeds rapidly when chloroform and sodium hydroxide are present in aqueous solution in the same concentration as they occur in blood during anæsthesia. It has been shown by experiments on dogs that the same reaction occurs in blood. No formates were detected in the urine during anæsthesia. W. O. W.

Physiological Action of Choline. LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*Zentr. Physiol.*, 1910, **24**, 251—253).—The greatest possible care was taken in the preparation of choline in a state of purity. The uniform result in anæsthetised, but not curarised, cats of intravenous injection was a temporary fall of blood-pressure, which does not occur after atropinisation. The original statements of Halliburton and Mott are thus confirmed. The contrary results described by Modrakowski could not be repeated (compare Abderhalden and Müller, this vol., ii, 530). W. D. H.

Caffeine Glycosuria. WILLIAM SALANT and G. W. KNIGHT (*Proc. Amer. Soc. Biol. Chem.*, 1909 ; *J. Biol. Chem.*, 1910, **7**, lii—liii).—In rabbits, glycosuria follows administration of caffeine within two or three hours, and lasts several, but not more than twenty-four, hours. The dose required is larger when given by the mouth. The effective dose is smaller when the diet is rich in carbohydrates, or when calcium chloride is also injected. Calcium chloride in itself produces no glycosuria. Similar experiments on dogs gave negative results. W. D. H.

The Cardio-vascular Action of Green Coffee Compared with that of Corresponding Doses of Caffeine. V. PACHON and EM. PERROT (*Compt. rend.*, 1910, **150**, 1703—1705).—The authors have

examined the physiological action of an extract of green coffee, in which the enzyme has been destroyed by alcohol. With dogs, intravenous injection caused marked lowering of the blood-pressure, followed by a gradual rise, and a diminution in the volume of the kidney. The administration of atropine did not influence these symptoms. Corresponding doses of pure caffeine produced no apparent effects. W. O. W.

The Presence in Ergot and Physiological Activity of β-Iminazoylethylamine. GEORGE BARGER and HENRY H. DALE (*Proc. physiol. Soc.*, 1910, xxxviii—xl; *J. Physiol.*, **40**).—The specific action on the cat's uterus produced by ergot is due to a base which was identified with β-iminazoylethylamine. This originates from histidine by the splitting off of carbon dioxide. W. D. H.

Action of Peptone Intravenously Injected in the Guinea Pig. A. BIEDL and R. KRAUS (*Zentr. Physiol.*, 1910, **24**, 258—261).—Peptone injection is toxic to the guinea-pig, the most marked result being spasm of the bronchial muscles. In dogs the effect is mainly paralysis of the smooth muscles, especially in the abdominal sympathetic area. The bronchial muscles are innervated by the vagus. The symptoms in the guinea pig are extremely similar to those seen in anaphylaxis. W. D. H.

The Effect of Inanition and of Various Diets on the Resistance of Animals to Certain Poisons. REID HUNT (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxix—xxx).—Marked variations occur in the resistance of mice, rats, guinea pigs, and dogs when fed on different diets, the poisons being morphine, cocaine, and acetonitrile. In extreme cases, the lethal dose was raised thirty times. These results are not due to the proportion of fats, carbohydrates, and proteins, but to specific effects of the foods. In one case, for example (the increased resistance of mice fed on oatmeal to acetonitrile), the effect seems to be due to the stimulation of growth in the thyroid which is produced by some substance in oatmeal. In some cases a restricted diet increased resistance. W. D. H.

Poisons and Enzymes. HUBERT W. BYWATERS and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlv—xlvii; *J. Physiol.*, **40**).—The suggestion has been made that the effect of certain alkaloids on muscle may be due to their action on enzymes. Aconitine, however, was found to have no action on ptyalin, and only a slight retarding action on invertase. W. D. H.

Serological Studies by means of the "Optical Method." X. EMIL ABDERHALDEN and LUDWIG PINCUSSOHN (*Zeitsch. physiol. Chem.*, 1910, **66**, 88—105).—The authors have investigated the action of a large number of toxins (diphtheria-, pyocyanase-, ricin-, cobra-toxin, etc.), and also of various sera, both normal and from animals undergoing immunisation, on different peptones, with the object of determining the activity of ferments. The changes of rotation were measured, and the results are plotted on thirty-seven plates. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Growth of Various Species of Bacteria and other Micro-organisms in Atmospheres Enriched with Oxygen. BENJAMIN MOORE and R. STENHOUSE WILLIAMS (*Bio.-Chem. J.*, 1910, **5**, 181—187).—Twenty-six varieties of organism were subjected to experiment; two of them, namely, those of tuberculosis and plague, stand out prominently as oxyphobic; the *Staphylococcus* growths were also adversely affected by increase of oxygen. The tubercle bacillus was killed by three weeks' exposure to a higher percentage of oxygen. The bacillus of plague was not killed by a few days' exposure to an oxygen percentage of from 60 to 90, but growth was arrested; longer times were not tried. W. D. H.

Utilisation of Amino-acids and Polypeptones by the Tubercle Bacillus. WILLIAM F. KOELKER and B. W. HAMMER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, li—lii).—Various amino-acid were added to the culture medium; there seems to be a difference in the behaviour of the homologous and the methyl-substituted amino-acids; thus glycine and alanine are favourable to the growth of the tubercle bacillus; amino*iso*butyric acid, valine, and leucine give no growth. The investigation with polypeptides is to be continued. W. D. H.

Chemical Reactions Occurring during Alcoholic Fermentation. IV. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1910, **43**, 1773—1795. Compare Abstr., 1904, ii, 199; 1905, ii, 274; 1906, ii, 790).—Lactic acid has been regarded as an intermediate product of alcoholic fermentation, partly owing to its appearance during fermentation with pressed yeast-juice. It was shown by Pasteur originally, and the fact has repeatedly been confirmed since, that lactic acid is never produced during fermentation with a pure living yeast.

As the result of a systematic and careful study of the behaviour of lactic acid towards living yeast, it is now shown that it is neither fermented nor produced during fermentation (compare Slator, Trans., 1906, **89**, 141; 1908, **93**, 231). Accordingly, the hypothesis that lactic acid is an intermediate product of fermentation is abandoned.

Methylglyoxal is not fermented either by living yeast or pressed yeast juice, neither can its formation be detected during the fermentation of sugar. Pure glyceraldehyde is slowly fermented by yeast to the extent of 10—25%. W. Löb (*Zeitsch. Elektrochem.*, 1907, **13**, 511) was unable to detect it as a product of fermentation. Dihydroxyacetone (compare Bertrand, Abstr., 1904, ii, 760) is fermented by pressed yeast juice in presence of sodium chloride to the extent of 80—90%. With living yeast, about 50% was fermented in twenty-four hours. Boysen-Jensen (Abstr., 1909, ii, 172) claims to have detected the formation of dihydroxyacetone during fermentation. The hypo-

thesis is advanced that dihydroxyacetone is to be regarded as the intermediate product of fermentation.

Glycerol is produced during fermentation with pressed yeast juice at the cost of the dextrose fermented, and is not formed from proteins or nuclein substances (compare Ehrlich, *Biochem. Zeitsch.*, 1909, **18**, 423).

Ethylideneoxyformate is not fermented by pressed yeast juice. A similar negative result is obtained with α-glucoheptose.

Sterilised 10% dextrose solution, preserved at the ordinary temperature for five years in sealed tubes, was found to have remained unchanged. E. F. A.

Formation of Acraldehyde in Bitter Wines. E. VOISENET (*Compt. rend*, 1910, **150**, 1614—1616).—Acraldehyde gives a bluish-green coloration with a solution of albumin containing hydrochloric and nitrous acids (Abstr., 1905, ii, 59 ; this vol., ii, 466). By applying this test, with others, acraldehyde has been detected in the distillate from bitter wines, and shown to be absent in that from normal wine. The aldehyde appears to be formed from the glycerol of wine, since it is produced when the bacteria causing bitterness are cultivated in an artificial medium containing 1% of glycerol. W. O. W.

The Production of Volatile Fatty Acids and Esters in Cheddar Cheese, and their Relation to the Development of Flavour. S. K. SUZUKI, E. G. HASTINGS, and EDWIN B. HART (*J. Biol. Chem*, 1910, **7**, 431—458).—Lactose disappears from Cheddar cheese in from three to six days; the lactic acid increases, and this increase after the disappearance of the lactose is probably of protein origin. The usual form of lactic acid is racemic. However, lactose solutions inoculated with *B. lactis acidi* produce the active acid, or when inoculated with a piece of the cheese a mixture of active and inactive acids is produced. No enzyme capable of producing lactic or volatile fatty acids from lactose could be isolated. Certain organisms in lactose solutions yield not lactic, but volatile fatty acids instead; the latter are also formed in the ripening of the cheese after lactose has disappeared; acetic, propionic, butyric, hexoic, but not valeric, acid were found. Formic acid was only found at the five and a-half months' stage. The principal sources of acetic and propionic acids are probably lactates; traces may come from protein or glycerol. The butyric and hexoic acids come from fats and proteins. The distillate ("flavour" solution) contained alcohols and esters; in mild cheeses these were mainly ethyl alcohol and ethyl acetate; in pungent cheeses mainly ethyl esters of hexoic and butyric acids. Succinic acid was also identified. W. D. H.

Influence of Humus on the Decomposition of Urea. HARALD R. CHRISTENSEN (*Centr. Bakt. Par.*, 1910, ii, **27**, 336—362).—Addition of a small amount of soil extract to a solution of urea containing the usual minerals failed to induce a production of ammonia, whilst the further addition of a little potassium humate soon caused a vigorous liberation of ammonia from the urea. Artificial humic acid from sucrose has a similar effect. Dextrose and various other non-nitrogenous carbon compounds give rise to ammonia production when

added to crude cultures of urea bacteria. With pure cultivations these substances (with the exception of calcium lactate) are only very slightly utilised, if at all.

Asparagine, and especially peptone, induce a vigorous production of ammonia when added to pure cultures of urea bacteria containing urea.

Solutions of urea containing no other carbon compound are readily decomposed with production of ammonia when inoculated from a fermented humin-urea solution. N. H. J. M.

Action of Ultra-violet Rays on (I) Certain Solutions Used in Pharmacy; (II) Certain Fatty Substances, Glucosides, Alkaloids, and Phenols. ANDRÉ LESURE (*J. Pharm. Chim.*, 1910, [vii], 1, 569—575, 575—576).—The object of this work was primarily to ascertain whether the sterilising action of ultra-violet rays could be used in rendering medicinal preparations, particularly those used for injection subcutaneously or otherwise, aseptic. Twenty-four different liquids were exposed during one to five minutes or fifteen to thirty minutes to the light emitted by a Cooper-Hewitt mercury lamp. The permeability to the rays was observed by their effect on sensitised paper after passing through the solution under observation. In most cases the permeability was comparable to that of water, but for solutions of atoxyl, caffeine, eserine salicylate, *apo*morphine hydrochloride, gentiopicrin, or olive oil it was from 1/10 to 1/5th that in water. With solutions of mercuric iodide (in sodium iodide), quinine dihydrochloride, or quinine disulphate, it was practically nil.

Certain of the solutions showed some change, thus silver nitrate, eserine salicylate, *apo*morphine hydrochloride, and atoxyl all became coloured after five minutes' exposure, whilst morphine hydrochloride, arbutin, and guaiacyl cacodylate developed colour after an exposure of from fifteen to thirty minutes. Olive oil was decolorised after illumination during thirty minutes, but there was no marked change in the constants of the oil.

A solution of aucubin containing *Bacterium coli* was completely sterilised in thirty seconds, but a similar preparation of gentiopicrin was not completely sterilised after thirty minutes' exposure.

In a second series of experiments, it was found that olive oil became acid after exposure during one hour, and that aucubin and gentiopicrin were decomposed and yielded reducing products after three hours.

Arbutin became very much coloured after three hours' illumination, due to formation of quinol and oxidation of this. Methylarbutin behaved similarly, but required longer exposure before coloration occurred. Quinol became coloured in five minutes, but methylquinol only after thirty minutes, and the solutions were then less permeable to the rays. Cocaine hydrochloride and pilocarpine hydrochloride did not appear to be affected appreciably even after three and a-half hours, although the latter became slightly coloured. T. A. H.

Selective Antiseptic Action of Copper Salts. ALFRED SPRINGER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxi—xxxii).—Copper salts are highly selective, being most

efficient in inhibiting the action of putrefactive organisms. This view is supported by some experiments on eggs, and the suggestion is made that the selective action may prove to be of therapeutic importance. W. D. H.

Composition of the Seeds of Cultivated Plants. ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1910, **73**, 35—170).—Results of analyses of seeds of various plants, including determinations of the proteins and other nitrogenous substances, constituents of ether extracts, soluble and insoluble carbohydrates, phosphorus compounds, and ash constituents.

The qualitative methods employed are described. N. H. J. M.

Chemical Organisation of a Typical Fruit. ALBERT E. VINSON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xl—xli).—Unripe dates of the invert sugar type contain high percentages of sucrose so long as the fruit remains intact. The fresh juice also contains appreciable amounts of sucrose, but this is rapidly hydrolysed to invert sugar in the presence of the pulp; this is due to the fact that when the tissues are crushed the intracellular invertase comes into contact with the sucrose. When filtered, the diastase remains with the pulp, but as the pressure employed during filtration is increased, larger quantities of soluble nitrogenous cell constituents make their way into the filtrate. J. J. S.

Ratio of Plant Nutrients as Affected by Harmful Soil Compounds. OSWALD SCHREINER and J. J. SKINNER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxxiii—xxxiv).—As the result of numerous experiments made by growing plants with varying amounts of phosphate, nitrate, and potassium fertilisers, both in the presence and absence of dihydroxystearic acid, it has been proved that the dihydroxy-acid greatly inhibits the plant growth, and that the effect is most marked where the ratios of the three fertilisers are least suited for growth. It is less harmful when the fertiliser is mainly nitrogenous than when mainly phosphatic or potassic, and the effect is also associated with a higher nitrogen removal.

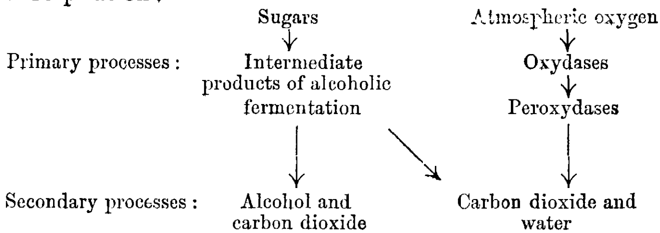
The amounts of potassium and phosphate removed were less in the presence of the dihydroxy-acid. J. J. S.

The Mechanism of the Oxidation of Sugar in Plant Respiration. S. KOSTYTSCHEFF (*Zeitsch. physiol. Chem.*, 1910, **67**, 116—137. Compare Abstr., 1909, i, 84, 173).—The readily oxidisable intermediate products formed during alcoholic fermentation can produce large quantities of carbon dioxide when treated with hydrogen peroxide and a ferrous salt. This was proved by using solutions which had been fermented by means of "hefanol," and were quite free from unaltered dextrose. As dextrose itself is readily oxidised by hydrogen peroxide and ferrous salts, it cannot be definitely stated, as the results of the above experiments, that zymase facilitates the oxidation of sugar. The same intermediate products also yield large quantities of carbon dioxide in the presence of hydrogen peroxide and

peroxydase from wheat seeds. Dextrose itself does not yield carbon dioxide under these conditions, and the intermediate products do not yield carbon dioxide with hydrogen peroxide alone. The preparations of oxydase also contain catalase, and the addition of hydrogen peroxide, not merely destroys the catalase, but also the peroxydase; the effects of the catalase are, however, largely negatived by the addition of potassium phosphate.

This is the first case in which carbon dioxide has been obtained from vegetable products by means of vegetable oxidising ferments.

The following scheme gives the main processes in the case of sugar respiration:



(compare Palladin, Abstr., 1909, ii, 511). The peroxydase functionates as an inductor, and not as a catalyst. J. J. S.

Concurrent Oxidising and Reducing Power of Roots. OSWALD SCHREINER and MICHAEL X. SULLIVAN (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxxii—xxxiii).—The roots of growing plants (such as wheat) can oxidise α-naphthylamine, benzidine, phenolphthalein, aloin, etc., and the oxidation is the most marked where the growth is greatest. Wheat roots grown in a solution of sodium selenite neutralised by hydrochloric acid, reduce the selenite, producing a pink deposit of selenium on the root; the reaction is most marked where the growth is vigorous. Roots killed by immersion in boiling water show no reducing action, and no reduction takes place in an alkaline selenite solution. In the main, with increased oxidising power, there is an increase in the reduction, whilst certain concentrations of potassium iodide retard oxidation, but either increase the reduction or have no effect. J. J. S.

Anæsthetics and Laurel Leaves. AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlix—li; *J. Physiol.*, **40**).—In chloroform vapour there is the greatest evolution of hydrogen cyanide, in ether less, in alcohol less still; in water there is none. The decline in electrical response follows the same order, being greatest in chloroform; in water there is no response. The evolution of the poison is a post mortem sign, and the enzyme that produces it may remain active for days in spite of the anæsthetic which kills the protoplasm. W. D. H.

Utilisation of Tricalcium Phosphate by Cruciferous Plants. CIRO RAVENNA and M. ZAMORANI (*Bied. Zentr.*, 1910, **39**, 495—496; from *Staz. sper. agrar. ital.*, 1909, **42**, 389).—Pot experiments in which mustard, vetches, and oats were grown in sand

manured with mono- and tri-calcium phosphate respectively in addition to other salts. In the case of mustard, the fresh produce was almost the same with tricalcium phosphate as with the monocalcium salt, whilst with vetches, and especially oats, there was less fresh produce with tricalcium phosphate. The dry matter results show that the greatest difference was with mustard, whilst the percentages of ash in the dry matter and of phosphoric acid in the ash were, like the fresh produce, almost the same with the two manures in the case of mustard, but distinctly lower as regards ash, and very much lower as regards phosphoric acid, with vetches and oats grown with tricalcium as compared with monocalcium phosphate. N. H. J. M.

The Action of Potassium Salts on the Formation of Sucrose in Seeds. G. DE PLATO (*Chem., Zentr.*, 1910, i, 1623; from *Staz. sper. agrar. ital.*, 1910, **43**, 97—104).—The author examined peas grown on different soils, and found that those coming from soils rich in calcium and potassium compounds contained in comparison with others from soils deficient in these constituents more carbohydrate, particularly sucrose, more potassium, calcium, and magnesium, but less nitrogenous substance. It appears that potassium favourably influences the production of carbohydrate, magnesium its transportation and storage in the seed, and calcium the formation of salts of organic acids. These are the three chief factors determining the high proportion of sugar in peas. E. J. R.

Presence of a Glucoside in the Leaves of the Pear Tree and its Extraction. ÉMILE BOURQUELOT and Mlle. A. FICHTENHOLZ (*Compt. rend.*, 1910, **151**, 81—84. Compare Rivière, Abstr., 1904, ii, 583).—Pear tree leaves contain a glucoside which is easily extracted by ethyl acetate, the yield amounting to 1·2—1·4%. The substance has m. p. 194—195°, $[\alpha]_D - 60{\cdot}38°$; it undergoes hydrolysis by emulsion, forming quinol, and is probably identical with arbutin. W. O. W.

The Preparation of Adenine from Beet Sugar Residues. KARL ANDRLÍK (*Zeitsch. Zuckerind. Böhm.*, 1910, **34**, 567—569).—To 1 part of the residues is added 2 of water and 0·1 of copper sulphate, after an hour's boiling, 0·03 of sodium hydroxide, and then the whole is boiled for half an-hour. The precipitate, separated by filtration through linen, is decomposed by hydrogen sulphide in presence of barium hydroxide (0·2—0·3 part for every 1 part of precipitate). After filtering, the clear liquid is saturated with carbon dioxide and evaporated to a syrup, when adenine separates out. Whether adenine exists as such in the residues or is a degradation product of nuclein is not ascertained, but 0·05% of pure adenine can be obtained from the residues. E. J. R.

The Presence of Allantoin in the Seeds of Datura Metel. G. DE PLATO (*Chem. Zentr.*, 1910, i, 1622; from *Staz. sper. agrar. ital.*, 1910, **43**, 79—85).—The seeds of *Datura Metel*, which are very

similar to those of *Nicotiana tabacum*, contain neither alkaloids nor cyanogenetic glucosides; they do, however, contain allantoin.

E. J. R.

Betaines which Occur in Plant Tissues. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **67**, 46—58).—Betaine, trigonelline, and stachydrine are the three betaines which have been isolated from plant tissues. They resemble one another in general chemical properties. The suggestion is made that they are much more widely distributed than is generally thought. They are regarded as waste products (Abfallstoffe) of vegetable metabolism.

Details for the isolation of these betaines and for their separation from other bases are given (compare Abstr., 1909, ii, 605). Care is required in the separation of stachydrine and choline, as stachydrine hydrochloride is appreciably soluble in cold absolute alcohol (1 in 12 or 13). When only small amounts of stachydrine are present, the separation is most readily effected by means of potassium tri-iodide in alkaline solution. Under these conditions, the choline is precipitated, but not the stachydrine.

The method of separating choline chloride from free stachydrine by means of mercuric chloride does not always give good results.

The aurichlorides are the best compounds to use for identifying stachydrine and trigonelline and the picrate for betaine.

J. J. S.

Production of Nicotine in Tobacco Culture. THÉOPHILE SCHLOESING, jun. (*Compt. rend.*, 1910, **151**, 23—26).—The results of experiments on a large scale are given in tabular form, the object of the inquiry being to ascertain the influence of cultural conditions on the yield of nicotine. Close planting tends to diminish the yield, whilst the proportion of sodium nitrate used as manure has little influence. Diminution of the number of leaves on the plant slightly increases the yield when this is expressed as a percentage of the dried material.

W. O. W.

Stachydrine and Other Bases Present in Stachys Tubers and in Citrus Leaves. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **67**, 59—96. Compare von Planta and Schulze, Abstr., 1893, i, 447, 679; Jahns, 1896, i, 712).—Full details are given for the isolation of stachydrine from the tubers of *Stachys tuberifera* and the leaves of *Citrus aurantium*. In the former case the yield of base is 0·18% of the dry substance, and small amounts of arginine, choline, trigonelline, and alloxuric bases are also present; together with glutamine and tyrosine. The yield from the *Citrus* leaves is much the same, and choline and alloxuric bases are also present.

The hydrochloride has m. p. 235° (decomp.), and one part dissolves in 12·58 parts of alcohol at 18°. The aurichloride has m. p. 225° when rapidly heated. The platinichloride forms a yellow, anhydrous precipitate from alcohol, or orange-red crystals containing $2H_2O$ from water. A third form, containing $4H_2O$ and crystallising in small aggregates, is

sometimes obtained. The mercurichloride is sparingly soluble. The *hydrogen oxalate*, $C_{17}H_{13}O_2N,H_2C_2O_4$, crystallises in needles, m. p. 105—107°, and the *sulphate*, $2C_{17}H_{13}O_2N,H_2SO_4 2H_2O$, is readily soluble in water. The methyl ester (Jahns, *loc. cit.*) is stable in acid solutions only. The *ethyl* ester is readily hydrolysed by potassium carbonate.

The precipitation of stachydrine by the addition of phosphotungstic acid to an aqueous solution of the hydrochloride of the base is not quantitative, and as much as 5% may remain in the filtrate. Similarly, the precipitation by means of mercuric chloride in either aqueous or alcoholic solution is not quantitative. Stachydrine can be identified by means of its characteristic aurichloride, and by the fact that the vapours given off when the base is heated in a glass-tube give a red coloration to a pine shaving moistened with hydrochloric acid.

The base is recovered unaltered in the urine after administration to the human system.

The constitution of stachydrine as the methylbetaine of hygric acid (Abstr., 1909, i, 324), $CH_2{<}{\begin{array}{l}CH_2\cdot CH\cdot CO\\ CH_2\cdot NMe_2 -\end{array}}{>}O$, has been confirmed by the conversion of the base into hygric acid, and also by its synthesis from this acid (this vol., i, 62). J. J. S.

Fixing and Staining Tannin in Plant Tissues. ALBERT E. VINSON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xli).—The tannin in vegetable cells, for instance, of dates and persimmons, is deposited and stained yellow by the vapour of ethyl or amyl nitrite. The specimen can be stained before being cut. For laboratory purposes a 20% solution of commercial ethyl nitrite in alcohol is recommended. J. J. S.

Chemical and Mycological Studies on a Corn Rot having Possible Relation to the Etiology of Pellagra. HOWARD S. REED (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, 1).—Maize when infected with pure cultures of *Diplodia zeae* and given to mice produced death in a few days. Chemical examination of the meal showed the presence of a substance soluble in alcohol, and resembling Lombroso's pellagrozein. Other crystalline substances have been isolated and their physiological properties examined. J. J. S.

The Nitrogen-free Extract of Soola Clover (Hedysarum coronarium). FRANCESCO SCURTI (*Chem. Zentr.*, 1910, i, 1632; from *Staz. sper. agrar. ital.*, 1910, **43**, 5—32).—The dry matter of Soola clover contains 46·38% of nitrogen-free extract, and this was more closely examined to determine its value. It is composed mainly of three groups: (1) true sugars, partly monosaccharides with 5 or 6 C atoms and partly disaccharides; (2) sugar anhydrides formed by condensation of the monosaccharides other than dextrose, which does not appear to come into this group; (3) acids, especially such as are formed from carbohydrates. The 46·38 parts of nitrogen-free extract are made up of 7·42 parts of dextrose, lævulose, and arabinose; 2·93 of sucrose; 3·73 of galactan, araban, etc., soluble in 0·06% of sodium hydroxide;

0·67 of free organic acid; 8·43 of other compounds acidic in nature; 23·2 of galactan, araban, etc., insoluble in alkalis, but hydrolysed by dilute sulphuric acid (determined by difference). E. J. R.

The Phosphorus of the Flat Turnip. BURT L. HARTWELL and WILHELM B. QUANTZ (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxxviii).—It appears that four-fifths of the phosphorus of flat turnips is present as soluble compounds, and exists mainly as inorganic phosphorus derivatives. The addition of 0·2% of hydrochloric acid to turnip juice renders it possible, after filtration, to precipitate practically all the phosphorus by the molybdic method. J. J. S.

Rate of Extraction of Plant Food Constituents from the Phosphates of Calcium and from Loam Soil. JAMES M. BELL (*J. Amer. Chem. Soc.*, 1910, **32**, 879—884).—In a recent paper (*Landw. Jahr.*, 1910, **39**, 299) on the rate of solution of two calcium phosphates and the rate of extraction of lime from a loam soil, by water saturated with carbon dioxide, Mitscherlich, Kunze, Celichowski, and Merres have come to the conclusion that the usual equation: $dy/dt = k(A - y)$ expressing the rate of solution does not accord with their data. These authors have, however, mistaken the significance of A, which represents the concentration of the solution when final equilibrium is reached. They have taken the value of A as the total quantity of the salt which was originally mixed with the carbonated water. The present author shows that the above equation gives good results when A is given its proper significance, although the phenomenon observed is not one of solution only, but also of hydrolysis. T. S. P.

Humic Acids of Grey Sand and Brown Sandstone. RICHARD HORNBERGER (*Landw. Versuchs-Stat.*, 1910, **73**, 221—233. Compare A. Mayer, Abstr., 1905, ii, 55).—Humic acid extracted from grey sand with sodium hydroxide contained from 62·4—64·6% of carbon. Extracts obtained with ammonia yielded humic acids containing 58·6—59·9% of carbon. Brown sandstone was found to contain humic acids with varying percentages of carbon, the higher percentages agreeing approximately with the lower percentages in humic acid from grey sand.

Whilst Mayer found that ferric chloride considerably reduced the percentage of carbon in humic acid from grey sand (from 59—40%), the results of numerous experiments failed to show any diminution.

As regards the production of brown sandstone, the results seem to indicate that ferric oxide is reduced by the humic acids of the grey sand and dissolved as ferrous humate (not oxyhumate), and that lower down it is oxidised to ferric humate, in which process there is not only a change from ferrous to ferric salt, but an oxidation of the acid as well, resulting in a lower percentage of carbon. It is assumed that the oxidation is accomplished in part by bacteria. N. H. J. M.

Analytical Chemistry.

Chemical Colour Reactions. C. REICHARD (*Pharm. Zentr.-h.*, 1910, **51**, 607—613).—A study of the nature of colour reactions The author summarises the results as follows: The value of a colour. reaction depends: (1) on the largest possible depth of colour in combination with purity of colour; (2) the highest sensitiveness; (3) a high degree of permanency. All these conditions become of the highest value in those cases where the reaction is associated with a quantitative formation of crystalline products. L. DE K.

Quantitative Application of the Theory of Indicators to Volumetric Analysis. ARTHUR A. NOYES (*J. Amer. Chem. Soc.*, 1910, **32**, 815—861. Compare Abstr., 1904, ii, 512; 1907, ii, 389).—A lengthy paper in which a quantitative development of the theory of indicators in a systematic form immediately applicable to the problems of volumetric analysis is given.

The equilibrium relations of the two differently coloured structural forms in which all indicators probably exist, and the equilibrium conditions under which such a pair of tautomeric substances can show sharply differentiated colours in acid and alkaline solution are first discussed. It is shown that, provided these conditions are fulfilled, the indicator can be treated in titrations as if it were a single acid or base having an ionisation constant which, although really a function of three equilibrium constants, can be directly determined either from the colour changes exhibited by it in solutions of various hydrion concentration, or by any of the other methods commonly applied, for example, by measurement of the conductivity of the indicator acid or base, or by a study of the hydrolysis of its salt.

The equilibrium relations of indicators with reference to the end-point of titrations are then formulated, the end-point (determined so as to correspond with a definite colour change) being reached when the hydrion concentration in the titrated solution attains a definite value. A number of lecture experiments illustrating the relation between the colour change of indicators and the hydrion concentration are then described, and the theory is then extended to deal with the following cases: (1) Titration of monobasic acids and monacid bases; limits beyond which the titration is impracticable. (2) Titration of two monobasic acids or of two monoacidic bases in the presence of each other. (3) Titration of dibasic acids with monacidic bases. (4) Titration of diacidic bases with monobasic acids.

In an appendix is given a summary of the values of the ionisation constants of various indicators and of various inorganic acids and bases. T. S. P.

Luteol [as an Indicator]. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, **67**, 115).—The use of luteol was first recommended by Späth as an indicator in the neutralisation of sulphuric acid containing ammonia. The end-point is the appearance of a yellow colour. Späth's statements on the advantages of luteol are confirmed. W. D. H.

Methylene-blue as Indicator in Iodometric Titrations. FRANK S. SINNATT (*Analyst*, 1910, **35**, 309—310).—When titrating with standard iodine, the usual indicator starch may be replaced by methylene-blue. A solution is made by dissolving 0·05 gram of the dye in a litre of water, and 1 c.c. of this is then added to 50 c.c. of the solution to be titrated. The end-point is noticed by the change from blue to yellowish-green. L. DE K.

Starch Indicator for Iodometric Titrations. L. MATHIEU (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 1166—1168).—A starch solution, which is free from undissolved starch grains and gives a clear blue coloration with small amounts of iodine, is prepared from soluble starch obtained by placing starch in contact with 0·1% hydrochloric acid for some length of time, then washing the mass, drying it at a temperature of 30°, and heating the dry powder for some hours at 100°. W. P. S.

Burette without Stopcock or Rubber Connexion. W. ALEXANDRON (*Zeitsch. anal. Chem.*, 1910, **49**, 436—437).—The apparatus consists of a calibrated tube drawn out to a fine point. To the upper part is sealed a bent tube about 5 mm. in width, and over this is pushed a long rubber tube furnished with a piece of tube drawn out to an opening 0 5 mm. diameter, and also with a pinchcock or screw clamp.

The burette is filled by suction and by means of the pinchcock; the flow from the burette is regulated. L. DE K.

A New Form of Extraction Apparatus. CHARLES WILSON GREENE (*J. Biol. Chem.*, 1910, **7**, 503—507).—A modification of Soxhlet's extraction apparatus is described and figured. W. D. H.

Two Cheap Appliances for Quantitative Work. [Supports for Crucibles.] KURT ARNDT (*Chem. Zeit.*, 1910, **34**, 649).—Old lids of porcelain crucibles, placed on wire gauze with a central hole, form convenient supports for platinum crucibles in the estimation of silica. Such lids, supported by fixing the handle in a slot in a matchbox, form convenient surfaces on which to rest hot platinum crucible lids. C. H. D.

[Laboratory Appliances for] Analytical Practice. CARL BEGER (*Zeitsch. anal. Chem.*, 1910, **49**, 427—436).—(1) When estimating the nitrogen in milks by the Kjeldahl process, it is recommended to wrap up the neck and part of the body of the digestion flask with lead foil. (2) For getting rid of the fumes when testing a number of samples, a system of lead tubes leading to a chimney has been found to act very satisfactorily. (3) Silver sand, so useful in the analysis of milk and excrement, should be tested for calcium carbonate, as this renders it unfit for use. (4) A kind of oil-cloth, black one side and green the other, is recommended instead of the usual black glazed paper in quantitative analyses. (5) An improved Kipp apparatus. The acid from the lower vessel, unless drawn off,

sometimes rises into the top one, and from there is ejected. By placing in the funnel tube of the top vessel a siphon, the other end of which is placed in a suitable vessel, the acid is removed automatically. (6) Application of Ostwald's thermo-regulator in artificial digestion. This thermo-regulator has been found very useful in digestion experiments with pepsin-hydrochloric acid at 38—40° (Stutzer's method), and may be recommended. L. DE K.

Microchemical Studies. IV. Refractive Indices of Crystalline Chemically Individual Substances by the Immersion Method as an Aid in Practical Analysis. A. BOLLAND (*Monatsh.*, 1910, **31**, 387—419. Compare Abstr., 1908, ii, 1080).—Tables are given of the refractive indices, determined by the immersion method, of a very large number of inorganic and of organic crystalline substances.

The inorganic substances are derivatives of nearly all the elements in the periodic table, whilst the organic compounds comprise hydrocarbons, iodine derivatives, alcohols, acids, aldehydes, ketones, and amides of the aliphatic series, and hydrocarbons, nitro-compounds, amines, phenols, alcohols, acids, aldehydes, and ketones of the aromatic series, and terpenes, glucosides, dyes, alkaloids, and various heterocyclic bases. C. S.

Estimation of Bromine in Monobromocamphor. ANDRÉ and LEULIER (*J. Pharm. Chim.*, 1910, [vii], **2**, 64—66).—The process is based on a reaction first noticed by Schiff, that monobromo-camphor dissolved in toluene yields sodium bromide on addition of metallic sodium.

0·5 Gram of the sample is placed in a 125 c.c. flask, 10 c.c. of toluene and 1 gram of metallic sodium are added, and the mixture is boiled for an hour, the flask being attached to an upright condenser. When cold, 30 c.c. of water are added to dissolve the excess of sodium, and, after acidifying strongly with nitric acid, 25 c.c. of *N*/10-silver nitrate are added, which precipitates the bromine as silver bromide. The excess of silver is then titrated by Volhard's method. The toluene does not cause any inconvenience. L. DE K.

Method for the Estimation of Sodium Iodide in Animal Tissues. PAUL J. HANZLIK (*J. Biol. Chem.*, 1910, **7**, 459—464).—The tissue is finely divided, mixed with 3—5 c.c. of 40% sodium hydroxide solution, dried at 100°, and then charred over a small flame. The residue is then oxidised by fusion with a mixture of equal parts of sodium nitrate and carbonate, which is added gradually. The mixture must not become red hot, as iodine is then lost. The white residue is extracted with water, the fitrate made up to a known volume, and an aliquot part (50 c.c.) taken for titration.

The 50 c.c. are agitated in a separating funnel with 10—15 c.c. of concentrated sulphuric acid; a small amount of sodium nitrite is added to complete the liberation of the iodine, which is extracted by shaking the liquid several times with chloroform (10 c.c.). The chloroform solution is shaken with water until free from acid, and is

then titrated with $N/10$-sodium thiosulphate solution. In control experiments, 97·8% of the iodide added was found by titration.

J. J. S.

Evaluation of Ammonium Hydrogen Fluoride. ERNST DEUSSEN (*Zeitsch. angew. Chem.*, 1910, **23**, 1257—1258).—Commercial acid ammonium fluoride is often composed of the normal salt, and should, therefore, be tested. The pure acid salt, however, loses some hydrogen fluoride on keeping.

0·05—0·08 Gram of the sample is placed in a 20 c.c. platinum dish, a few drops of water are added, and then about 9 c.c. of standard barium hydroxide. After remaining overnight, the dish being covered with a watch-glass and placed under a bell-jar, it is placed on the water-bath and heated for four to five hours. The liquid is then transferred to a beaker, the dish is slightly rinsed, and the solution is boiled until every trace of ammonia is expelled. The dish is now rinsed with a definite amount of N-hydrochloric acid and then with water, the liquids being added to the contents of the beaker. After heating for some time, adding more acid if required, the excess of acid is titrated with standard barium hydroxide, with phenolphthalein as indicator. The result equals total fluorine. L. DE K.

Estimation of Dissolved Oxygen in Waters. WILLEM P. JORISSEN (*Zeitsch. anal. Chem.*, 1910, **49**, 424—427).—Romyn (Abstr., 1896, ii, 579) devised a process which was briefly as follows. To the water collected in a special pipette is added sodium potassium tartrate, a solution of manganous chloride, and potassium iodide. aqueous sodium hydroxide is added, and, after some time, the solution is acidified, and the iodine liberated, representing the oxygen, is titrated.

The author states that, although this process gives trustworthy results with soft drinking waters, it fails with sea-water or other brackish waters, the results being far below the actual amount present. L. DE K.

New Apparatus for the Estimation of Sulphur and Arsenic. A. KLEINE (*Chem. Zeit.*, 1910, **34**, 636—637).—Several modifications of the apparatus are described. For the estimation of sulphur in mild steel, dilute hydrochloric acid is used, and the gases evolved pass through a condenser with an internal glass spiral. For cast-iron and steels high in carbon, concentrated hydrochloric acid is used, and the gases pass through a spiral washing vessel placed inside the condenser. A simplified form is described for technical use.

A distillation flask which dispenses with the usual ground-in funnel is described for the estimation of arsenic. The flask and funnel are blown in one piece, the funnel being closed by a rod.

C. H. D.

Estimation of Combustible Sulphur in Graphite. J. CIBULKA (*Chem. Zeit.*, 1910, **34**, 757).—0·5 Gram of the sample is weighed in a platinum boat, which is then placed in a combustion tube and

heated to redness in a slow current of dry oxygen. The products of the combustion are absorbed in a 10-bulb apparatus containing 20 c.c. of water and 20 c.c. of 3% hydrogen peroxide. The sulphuric acid formed is afterwards titrated with *N*/10-sodium hydroxide, using methyl-orange as indicator. Any acidity present in the hydrogen peroxide must be allowed for. L. DE K.

Detection of Small Quantities of Sulphur in Inorganic and Organic Compounds. ERNST DEUSSEN (*Zeitsch. angew. Chem.*, 1910, **23**, 1258—1260).—The substance, for instance, a couple of barley grains, is powdered and mixed with 0·1 gram of sodium carbonate and the small cuttings or scrapings of a filter 9 cm. in diameter. A few c.c. of water are added, and the mass evaporated over a spirit flame. When dry, the residue is well rubbed by means of a pestle with another 0·2 gram of sodium carbonate. The mass is now introduced into a 5 cm. long filter paper cartridge, which is then wound round three or four times with a platinum wire attached to a glass rod. The cartridge is then heated for six to ten minutes in the inner flame of the blowpipe, the source of heat being Kahlbaum's "molecular" benzene, which is absolutely free from sulphur. The fused mass is then dissolved in water and the filtrate tested for sulphide by means of alkaline lead acetate (10 drops *N*-lead solution, 70 c.c. water, 20 c.c. *N*-sodium hydroxide); 0·01 mg. of SO_4 may be detected by the process; it is obvious that a blank experiment should be made to ascertain the purity of the materials used. If fluorides are also present, the process is as follows. The soda-mixture (about 0·2 gram) is treated with a few drops of water and absorbed in filter paper, which is then dried on the water bath. The paper is then cut up and placed in a 2—3 cm. long paper cartridge, which is then wound round with platinum wire attached to a glass rod. After first charring the cartridge over a spirit-lamp, the cinder is heated in the inner flame of the blow-pipe burner for about ten minutes, when the usual lead test is applied.

The author criticises Ehrenfeld's and Indra's process for the detection of sulphuric acid in presence of fluorides (Abstr., 1909, ii, 438) adversely, as zinc dust always contains sulphur, and, therefore, cannot be used for reduction purposes. Kahlbaum's zinc powder, however, is free from sulphur. L. DE K.

Volumetric Estimation of Combined Sulphuric Acid by the Barium Chromate Method. HEINRICH ROEMER (*Zeitsch. anal. Chem.*, 1910, **49**, 490—492).—A slight modification of the barium chromate process suitable for the estimation of sulphates in commercially pure samples of potassium chloride. Fifty grams of the salt are dissolved in 150 c.c. of hot water, and 4 c.c. of hydrochloric acid and 10 c.c. (or more) of *N*/2-barium chloride are added. When cold, a corresponding amount of potassium dichromate solution is added, and a sufficiency of ammonia to precipitate the barium chromate. The chromate remaining in the liquid, which represents the sulphate, is then titrated either by the ferrous sulphate process or the iodometric method.

The process can, of course, be used in the analysis of waters, etc. For large quantities of sulphates, Wildenstein's chromate process (*ibid.*, 1862, i, 323) is recommended. L. DE K.

Kjeldahl Estimations of Nitrogen. EDWARD F. HARRISON and PERCY A. W. SELF (*Pharm. J.*, 1910, [iv], **31**, 4).—In order to avoid fixed alkali being carried over into the ammoniacal distillate, the authors operate as follows:

The acid liquid (25 c.c. of sulphuric acid are used for the Kjeldahl digestion) is diluted and transferred to a long-necked, 1-litre balloon flask containing two or three pieces of granulated zinc; this is closed with a rubber cork carrying a tapped funnel and a drip-head of about 80 c.c. capacity, the latter being connected to a block-tin tube passing through a Liebig's condenser, and the other end of which dips into a measured quantity of standard acid. A sufficiency of aqueous sodium hydroxide and then more water are introduced into the flask until the total volume is about 700 c.c., and when distillation commences the distance from the top of the liquid to the bottom of the drip-head should be eight inches, and from the bottom of the drip-head to the bend where it enters the condenser also eight inches. The distillation is now carried on vigorously for forty-five minutes; on heating further, more and more alkali is carried over.

It is as well to make a blank experiment and to apply the slight correction indicated. L. DE K.

Estimation of Total Nitrogen by means of Formaldehyde Titration. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, **67**, 1—7).—The following method is recommended for estimating the total nitrogen in urine. Phosphates are first removed by precipitating as ferric phosphate in the presence of acetic acid, the excess of iron is removed as basic ferric acetate, and a portion of the filtrate is heated with sulphuric acid, potassium sulphate, and copper sulphate in a Kjeldahl flask. The copper is subsequently removed as sulphide by the addition of sodium sulphide, and the excess of hydrogen sulphide boiled off. The filtrate is then neutralised with sodium hydroxide, using three drops of phenolphthalein as indicator, and the ammonium salts then estimated by Sörensen's "formaldehyde titration" method (Abstr., 1908, i, 115; ii, 234).

Good results cannot be obtained by rendering the acid solution neutral to litmus before adding the formaldehyde solution.

J. J. S.

Method for Estimating Amino-nitrogen, and its Applications. DONALD D. VAN SLYKE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxxiv–xxxvi).—An amine or amino-acid reacts with nitrous acid, liberating free nitrogen; in the method described, this nitrogen is liberated in an atmosphere of pure nitric oxide, which is afterwards absorbed by alkaline permanganate and the pure nitrogen then measured in a gas-burette. Good results have been obtained with alanine, valine, leucine, glycine, aspartic acid, glutamic acid, phenylalanine, serine, oxyproline, tyrosine, arginine, histidine, tryptophan, leucylleucine, leucylglycine, cytosine, guanine,

and lysine (2 mols. N). Proline and glycine anhydride, which contain imino-nitrogen, do not react. Guanidine and creatine do not react, nor does the amide-nitrogen of asparagine.

The method can be used for identifying amino-acids, for determining the degree of completeness of hydrolysis of proteins, and for accurate determination of the proline obtained by the ester method. In the mixture of esters boiling below 100°, the total N is determined, and also the amino-N; the difference gives the nitrogen present as proline. Histidine and arginine can be identified without isolation, and the amino-nitrogen present in urine can be determined after destruction of the ammonia and urea. J. J. S.

Estimation of Nitrates. CLARENS (*J. Pharm. Chim.*, 1910, [vii], 1, 589—593).—The process depends on the reduction of nitric acid by mercury or copper powder in the cold and the measurement of the nitric oxide produced.

The ureometer already described (Abstr., 1909, ii, 826) is used for the estimation. The pipette of the instrument is first filled with the solution to be investigated. In the reaction flask is placed sulphuric acid diluted with half its volume of water and copper powder in excess. The flask is then closed and placed in a water-bath kept at atmospheric pressure. The air in the flask is replaced by hydrogen by connecting the third tube in the stopper to a hydrogen apparatus, and finally the third tube is connected to the pipette containing the nitrate solution, the pressure in the flask being at the same time made equal to that of the atmosphere by adjusting the manometer. The nitrate solution is now run into the flask, the latter being slightly shaken to facilitate the reaction, which is over in a few seconds. The volume of gas produced is determined by the change in pressure in the manometer. The apparatus is first calibrated by making a determination with a nitrate solution of known strength.

For an apparatus of 130 c.c. capacity and a pipette holding 4 c.c., it is convenient to use nitrate solutions containing 2 to 4% of nitrates.

T. A. H.

Pozzi-Escot's and Devarda's Methods for the Estimation of Nitrates. EDWARD CAHEN (*Analyst*, 1910, **35**, 307—308).—Pozzi-Escot's method for the reduction of nitric nitrogen to ammonia (use of aluminium-mercury couple: this vol., ii, 155) is untrustworthy, but, with a slight modification, Devarda's aluminium process gives good results.

The solution of the nitrate is treated in a Jena distilling flask with 2 to 3 grams of an alloy composed of 45 parts of aluminium, 5 parts of zinc, and 50 parts of copper. Fifty c.c. of strong aqueous sodium hydroxide are added, and the flask is at once connected to the Kjeldahl distilling apparatus. After thirty minutes, when the reduction is complete, the contents are heated to boiling, and the ammonia is distilled in a current of steam and absorbed in standard acid as usual. Methyl-red is recommended as a suitable indicator. L. DE K.

Estimation of Phosphoric Acid by means of Standard Silver Nitrate. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, **29**, 794—796).—A slight modification of Holleman's silver process. The

phosphoric acid solution is rendered slightly alkaline with sodium hydroxide, using phenolphthalein as indicator, and the pink colour is then discharged with dilute nitric acid. A sufficient amount of *N*/10-silver nitrate is added, and then 10 c.c. of *N*/10-sodium acetate, and the pink colour is restored by cautiously adding *N*/10-sodium hydroxide; the final adjustment is then made with *N*/10-sulphuric acid. After diluting the whole to 150 c.c. and thoroughly shaking, the silver phosphate is removed by filtration, and in 100 c.c. of the filtrate the excess of silver is estimated by Volhard's thiocyanate process.

The process works well for calcium phosphates, but not with phosphates containing iron or aluminium. L. DE K.

Analysis of Commercial Phosphates. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, **29**, 796—799).—6·206 Grams of the phosphate are dissolved in nitric acid and diluted to 500 c.c. Ten c.c. (0·1241 gram) are transferred to a dish and evaporated nearly to dryness on the water-bath with addition of 5 c.c. of *N*-sulphuric acid. When the nitric acid has been expelled, a little water is added, and the whole again evaporated; the contents are transferred to a Jena flask by means of water, and 24 c.c. of *N*/10-silver nitrate are added. The liquid is then titrated with *N*/10-barium hydroxide, using phenolphthalein as indicator. After adding 30 c.c. of *N*/5-sodium acetate, 10 c.c. of the solution are transferred to a 150 c.c. flask, and a little water, also a few drops of phenolphthalein, are added. Sodium hydroxide solution is added until a permanent precipitate is formed, which is then redissolved by addition of a few drops of dilute nitric acid; on adding 25 c.c. of *N*/10-silver nitrate, the liquid should remain clear. Ten c.c. of *N*/10-sodium acetate are now added, and then *N*/10-sodium hydroxide until a permanent pink colour is just developed; 2 c.c. of *N*/10-sulphuric acid are added, and the whole is diluted to 150 c.c. After thorough mixing and filtering, the excess of silver is estimated in 100 c.c. of the filtrate by Volhard's method.

If b c.c. of *N*/10-barium hydroxide have been used in the first titration (allowing for the sulphuric acid added), and S c.c. of silver nitrate in the second, then:

$$\%\mathrm{CaO} = (S - b)\ 0{\cdot}002805 \times 100/0{\cdot}12412 = (S - b)\ 2{\cdot}26.$$
$$\%\mathrm{P_2O_5} = S \times 0{\cdot}002367 \times 100/0{\cdot}12412 = S \times 1{\cdot}907.$$

If b is less than $S/3$, the only constituents are the *di-* and *tri*-phosphates, and these may be expressed as:

$$\%\text{ of } \mathrm{CaHPO_2} = b \times 0{\cdot}1361 \times 100/0{\cdot}12412 = b \times 10{\cdot}966.$$
$$\%\text{ of } \mathrm{Ca_3P_2O_8} = (S - 3b)\ 0{\cdot}00517 \times 100/0{\cdot}12412 = (S - 3b)\ 100/24.$$

In this process any chlorides must either be expelled or otherwise allowed for, and such substances as bone-meal should be ignited previously to solution. L. DE K.

New Calcium Chloride U-Tube. RICHARD MÜLLER (*Chem. Zeit.*, 1910, **34**, 649).—In order to lessen the liability to breakage, the two arms of the U-tube are bent so as to be in contact at the stoppered ends. C. H. D.

Decomposition of Carbonates by Heating with Sodium Metaphosphate. WILHELM BÖTTGER (*Zeitsch. anal. Chem.*, 1910, **49**, 487—489).—Sodium metaphosphate, prepared by fusing sodium-

dihydrogen phosphate at a faint red heat until the weight is constant, is recommended instead of borax glass in the analysis of carbonates (estimation of carbon dioxide). Porcelain crucibles are not suitable for this process. L. DE K.

Electroanalysis. FREDERIC S. KIPPING, FREDERICK M. PERKIN, GEORGE T. BEILBY, THOMAS M. LOWRY, WILLIAM J. POPE, and HENRY J. S. SAND (*Brit. Assoc. Report*, 1909, 144—145).—This report deals with the estimation of mercury by electro-deposition on gold, silver, platinum, and mercury cathodes. It is found that satisfactory results are only obtained when a mercury cathode is employed; with the other metals the results are almost invariably too high.

E. H.

Analysis of Copper-Manganese Alloys. Direct Titration of Iron and Manganese Present in the Same Solution. E. AZZARELLO (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 552—555).—The following method has proved to be rapid and accurate for the analysis of alloys containing about 95% copper, 4·5% manganese, and smaller quantities of iron and lead. The alloy is dissolved in nitric acid, and the latter is then driven off by heating with sulphuric acid, and in the acid solution, previously warmed to 60°, the copper is estimated by electrolysis with a current of 0·3—0·27 ampere per sq. dcm. at 1·7—2·5 volts. The solution is treated with small quantities of 3% hydrogen peroxide to dissolve any precipitate of oxides of iron and manganese, and to destroy any permanganic acid which may have been formed. The excess of hydrogen peroxide is removed by the addition of the requisite quantity of *N*/100-permanganate, and the liquid is reduced with zinc and titrated with permanganate. When the iron has been estimated in this way, the greater part of the acid is neutralised with sodium hydroxide, a slight excess of zinc oxide is added, and the manganese in the solution is then titrated with *N*/10-permanganate, allowance being made in the calculation for the manganese which has been added in the previous titrations. R. V. S.

Volumetric Estimation of Manganese. Z. KARAOGLANOFF (*Zeitsch. anal. Chem.*, 1910, **49**, 419—424).—A modification of Volhard's method (hot titration of manganous sulphate with permanganate in presence of zinc sulphate) which does not work well in presence of iron, and has also other drawbacks. If, however, instead of the sulphate, the nitrate is taken, and about twice or thrice the weight of ferric nitrate is added, the titration gives good results. Instead of ferric nitrate, silver nitrate may be used with advantage for rapid work.

Very unfavourable results are obtained by using free nitric acid or zinc, aluminium, or barium nitrates, or by simply titrating the manganous nitrate without an additional salt. L. DE K.

Rapid Method for the Detection and Colorimetric Estimation of Small Quantities of Vanadium in Steel. PAUL SLAWIK (*Chem. Zeit.*, 1910, **34**, 648).—For the detection of vanadium in steel,

0·25 gram of turnings is dissolved in 4 c.c. of nitric acid, D 1·20, and warmed; 0·3 gram of solid ammonium persulphate is then added, and, after heating until the evolution of gas ceases, the tube is cooled. On the addition of 3 to 4 c.c. of phosphoric acid, D 1·30, the yellow colour of the iron disappears, and the solution is pale pink. After stirring, 3 to 4 c.c. of hydrogen peroxide are run in down the side of the tube from a pipette. A reddish-brown ring is formed, even by 0·01% of vanadium. The method becomes a quantitative one for steels containing less than 0·5% of vanadium, a steel of known content of vanadium being used as a colorimetric standard, or a steel free from vanadium, together with a dilute titrated solution of vanadium, may be employed.

For the exact estimation of vanadium in steel, 20 grams of turnings are dissolved in 60 c.c. of sulphuric acid, D 1·20, and 200 c.c. of water, and the solution nearly neutralised while hot with zinc oxide, the neutralisation being completed by adding zinc oxide, freshly precipitated with ammonia, until a slight turbidity remains. After boiling for fifteen minutes in a covered beaker, the precipitate, containing the vanadium and a little iron, is collected, washed with hot water, dried, and ignited. It is then fused with sodium hydroxide and potassium nitrate, dissolved, and filtered. The vanadium is best estimated in the filtrate by precipitating with manganous chloride, dissolving the precipitate in hydrochloric acid, heating with sulphuric acid, and titrating with potassium permanganate. C. H. D.

Separation of Bismuth from Lead and the Analysis of Bismuth-Lead Alloys. Harry F. V. Little and Edward Cahen (*Analyst*, 1910, 35, 301—306).—The process recommended by Benkert and Smith (double precipitation as bismuth formate: Abstr., 1897, ii, 435) is found to give good results. When applying this to commercial alloys, the authors operate as follows:

0·5—0·7 Gram of the sample is dissolved in a little nitric acid diluted with water, and any precipitate is collected, washed with hot dilute nitric acid (1 : 2), and then with water. It is then rinsed into a beaker with a little water, and heated for a few minutes with 25 c.c. of ammonium hydrosulphide. The solution is then filtered through the same filter, and the insoluble sulphides, after being washed, are dissolved in a little nitric acid, and the solution added to the main filtrate. This is then evaporated to a small bulk to expel most of the nitric acid, and, after neutralising as far as possible with solution of sodium carbonate, the bismuth is removed by boiling with sodium formate; to completely free the precipitate from lead, a second treatment with sodium formate is necessary. The bismuth is finally weighed as phosphate according to Stähler's method (Abstr., 1907, ii, 655).

In the filtrate from the bismuth, the lead is estimated in the usual way as sulphate; the filtrate contains any cadmium which may then be precipitated as carbonate, and weighed as oxide, or it may be deposited electrolytically in presence of potassium cyanide. The tin may be deposited electrolytically from its ammonium sulphide solution, or else converted as usual into oxide. L. de K.

Estimation and Separation of Palladium. ALEXANDER GUTBIER and FERDINAND FALCO (*Zeitsch. anal. Chem.*, 1910, **49**, 492—493).—A correction of some statements in the authors' paper on this subject (this vol., ii, 459). L. DE K.

Method for the Complete Extraction of Chloroform Vapour from Air and for its Estimation. MAURICE NICLOUX (*Bull. Soc. chim.*, 1910, [iv], 7, 561—567).—The air containing chloroform vapour is drawn by means of an aspirator up a glass-tube 1 metre long and 30 mm. wide, filled with glass balls, 3—5 mm. in diameter. Alcohol is allowed to run slowly down this tube, and in this the chloroform vapour dissolves, and the solution is collected in a bottle at the base of the tube. A wash-bottle containing alcohol may be inserted before the extraction tube, so that the rate at which the air is drawn through may be estimated roughly. Finally, the alcohol in the wash-bottle is mixed with that in the receptacle, and the whole boiled with potassium hydroxide in a reflux apparatus, and the potassium chloride formed by the decomposition of the chloroform estimated by Mohr's method after exact neutralisation. Air containing chloroform may be passed through this apparatus at the rate of 80 to 100 litres per hour without loss of chloroform. The apparatus may prove useful for other quantitative gas absorption work (compare Davis, Abstr., 1909, ii, 615). T. A. H.

Refractive Indices of Water-Alcohol Mixtures. D. SIDERSKY (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 1168—1169).—The refractive index of a mixture of alcohol and water increases in proportion to the alcohol-content, the increase being about 0·0005 per degree of the Gay Lussac scale. A maximum value is reached at a concentration of 85·69° Gay Lussac, the mixture then having $n_D^{27.5}$ 1·36587; the value then diminishes as the percentage of alcohol increases, absolute alcohol having $n_D^{27.5}$ 1·36229, a value also shown by a mixture reading 59·23° Gay Lussac. Solutions containing more than 50% of alcohol should, therefore, be diluted with a known quantity of water before the alcoholic strength is estimated by means of the refractometer (compare Abstr., 1907, ii, 821). W. P. S.

New Method for the Estimation of Glycerol in Wines. CONSTANTIN BÉYS (*Compt. rend.*, 1910, **151**, 80—81).—Fifty c.c. of wine (25 c.c. if the density is less than 5° Beaumé) are neutralised with barium hydroxide and concentrated, below 70°, to a syrup. Sand is added, and the glycerol extracted with 40—50 c.c. of acetone on a water-bath below 56°. The process is repeated until the filtered liquid amounts to at least 200 c.c. Two aliquot portions are evaporated without boiling, and the sugars determined in one by Fehling's solution. The other portion is dissolved in five times its weight of water, and treated with solid barium hydroxide (4/5th of the weight of the sugar). Sand is then added, and the mixture extracted four times with 25 c.c. of acetone. The extract is evaporated at 56°, dried at 60—65°, and weighed. If the wine contains less than 5% of sugar, the first extraction is unnecessary. W. O. W.

Potassium Ferrocyanide as an Indicator in the Estimation of Dextrose. ETTORE SELVATICI (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 1179—1184).—The following manner of employing potassium ferrocyanide as an indicator of the end-point of the titration of Fehling's solution with dextrose solutions is recommended. Ten c.c. of Fehling's solution, 10 c.c. of water, and 10 c.c. of a 1·5% potassium ferrocyanide solution are placed in a test-tube 25 cm. long and 3 cm. in diameter, boiled, and the dextrose solution is run in from a burette, the contents of the tube being maintained at a boiling temperature during the whole of the time taken for the titration. When all the cupric salt has been reduced by the added sugar, the mixture becomes quite colourless. W. P. S.

Bang's Method of Estimating Sugar, and the Preservability of the Reagents Employed in Titration. A. C. ANDERSEN (*Biochem. Zeitsch.*, 1910, **26**, 157—164).—It was found that Bang's hydroxylamine solution can be kept without appreciable change for prolonged periods if protected from light, whereas the copper solution undergoes change when kept both in the light and in the dark, and more rapidly in the former condition than in the latter. S. B. S.

Colorimetric Method of Estimating Small Quantities of Sugar by means of the α-Naphthol Test. ROBERT FRAILONG (*Bull. Assoc. chim. Sucr. Dist.*, 1910, **27**, 1188—1190).—The author recommends the preparation of photographic standards for use in comparison; for this purpose, solutions containing known quantities of sugar are treated with the reagent and sulphuric acid, definite proportions of each being employed (2 c.c. of sulphuric acid, 1 c.c. of the sugar solution, and 4 drops of a 2·5% α-naphthol solution). The colorations produced are then suitably illuminated and photographed on an autochromatic plate (Lumière). The coloration obtained with any sugar solution under examination is compared with these photographic standards. W. P. S.

Estimation of the Total Soluble Fatty Acids in Fats. ALBERT BRUNO (*Ann. Falsif.*, 1910, **3**, 238—239).—The process described is a continuation of the method usually employed for the estimation of the saponification number of fats. After the final titration, the addition of the titration acid is continued until a quantity, exactly equivalent to the amount of alkali used, has been added to the solution. Hot water is then added to the mixture (which should be contained in a flask graduated at 151·8 c.c. at a temperature of 50°) until the volume of the whole measures 151·8 c.c. at 50°. After mixing, the liquid is cooled, filtered, and the soluble fatty acids are titrated in an aliquot portion of the filtrate.
W. P. S.

A New Method for Estimating Fat and Fatty Acids in Fæces. OTTO FOLIN and A. H. WENTWORTH (*J. Biol. Chem.*, 1910, **7**, 421—426).—The dried material is pulverised and extracted with a mixture of ether and hydrochloric acid for twenty hours; the residue

of the extract is extracted with light petroleum, and the residue of this extract is weighed; this gives the total weight of neutral fats and fatty acids. It is dissolved in benzene, a few drops of 0·5% alcoholic solution of phenolphthalein added, and the mixture heated to near its boiling point. It is then titrated with a standard sodium ethoxide solution until the maximum colour of the indicator is obtained; this gives the total fatty acid (both that free and that present in the form of soaps). The neutral fat is obtained by subtracting the value of the second estimation from the first. It is not regarded as possible to determine the free fatty acids and the soaps separately. Increase in the total fats of the fæces is mainly due to increase of the fatty acid, and this is mainly stearic acid. W. D. H.

A Simple Apparatus for Bromination. HENRIK BULL and LELF SAETHER (*Chem. Zeit.*, 1910, **34**, 649).—The apparatus is specially designed for the preparation of the bromides of unsaturated fatty acids. The brominating flask is placed in an inclined position, and is provided with a glass tubular stirrer, expanded into a spoon at the lower end and slightly bent. The stirrer is fitted with a pulley and is mechanically driven, and the bromine is allowed to fall through it from a capillary tube, so that 1 c.c. is admitted in about eight minutes. Control analyses are given to show the accuracy of the estimation of unsaturated acids by means of it. C. H. D.

Estimation of Tartaric Acid in Wine Products. CONSTANTIN BÉYS (*Bull. Soc. chim.*, 1910, [iv], **7**, 697—699).—The process is designed to avoid the errors of Goldenberg and Géromont's method (Abstr., 1898, ii, 465, 545), and depends on the decomposition of the crude tartrate with hot dilute sulphuric acid, extraction of the tartaric acid by means of a mixture of alcohol and ether, decomposition of any ethyl tartrate formed by ebullition with excess of potassium hydroxide in alcohol, and precipitation of the tartaric acid as potassium hydrogen tartrate by the addition of acetic acid. The precipitated tartrate is finally titrated with standard alkali, using phenolphthalein as indicator. Precise details and quantities of reagents to be used are given in the original. T. A. H.

Conventional Methods for the Analysis of Materials [Tartrates] Adopted by the Seventh International Congress of Applied Chemistry. P. CARLES (*Bull. Soc. chim.*, 1910, [iv], **7**, 586—588).—From a thoroughly representative sample of known weight the grosser impurities are picked out and weighed. The residue is broken up so as to pass through a 0·5 mm. sieve and then ground. The potassium hydrogen tartrate is determined by placing 2·35 grams in 400 c.c. of water in a 500 c.c. flask, boiling for five minutes, cooling, and making up to 500 c.c. The flask is then shaken, and the contents filtered. Of the filtrate, 250 c.c. are heated to boiling in a porcelain dish and titrated, using *N*/4-potassium hydroxide with litmus paper as indicator, a similar determination with pure potassium hydrogen tartrate being made at the same time as a control.

For the estimation of "total tartaric acid," 6 grams of material

containing over 45%, or 12 grams of poorer material are thoroughly mixed with 18 c.c. of hydrochloric acid (D 1·10) in a 200 c.c. beaker, macerated during ten to fifteen minutes, washed into a measuring flask, made up to 200 c.c., and 100 c.c. collected in a dry, conical flask, after filtration through dry paper. This is heated to boiling, and 10 c.c. of a solution of potassium carbonate (D 1·49) added gradually. The mixture is shaken, slowly heated, and finally boiled during twenty minutes. The contents are then cooled, made up to 200 c.c., filtered through dry paper, and 100 c.c. of the filtrate are evaporated to 15 c.c. in a porcelain capsule. To this, 3·5 c.c. of glacial acetic acid are added in drops, and the mixture stirred during five minutes. After ten minutes, 100 c.c. of alcohol of 95° are added with continuous agitation, and, after standing ten minutes, the precipitate is collected, washed with alcohol until the latter is no longer acid, and the filter paper and precipitate transferred to a porcelain capsule containing 200 to 300 c.c. of water, boiled, and then titrated with *N*/4- or *N*/5-potassium hydroxide solution, using litmus paper as indicator. Deduction must be made from the percentage of "total acid" found, for insoluble matter not reckoned in making up the volume of the solution; the corrections are given in brackets after the percentages to which they correspond: 20 (0·8), 30 (0·7) 40 (0·6), 50 (0·25), 60 (0·15), 80 (0·10).

T. A. H.

Detection of Glycuronic Acid in Urine. GUIDO GOLDSCHMIEDT (*Zeitsch. physiol. Chem.*, 1910, **67**, 194).—The author's test for glycuronic acid (this vol., ii, 555) is interfered with by the presence of nitrates, which by themselves give a very similar colour. Röhmann has described nitrates in human urine, which come from the food, but they are absent from the urine of rabbits and dogs. In man, a nitrate-free diet can easily be adopted in laboratory and clinical work. In the present research no nitrates were found in the urine of man, cat, dog, or rabbit.

W. D. H.

Estimation of Hydrocyanic Acid in the Blood and Tissues After Death. AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlvii—xlix; *J. Physiol.*, **40**).—The method is colorimetric, and is based on the method of Hlasiwetz as recently applied by Guignard. A colour scale is prepared by mixing dilute hydrocyanic acid and picrate mixture in various concentrations, and the estimation is made by matching the colour given by the fluid under investigation, or of its distillate, with picrate mixture, with that of the colour scale.

W. D. H.

Estimation of Benzoic Acid in Foods. FOEKE H. VAN DER LAAN and H. TYDENS (*Chem. Weekblad*, 1910, **7**, 603—615).—Fifty to seventy c.c. of the aqueous alkaline extract are acidified with dilute sulphuric acid, a few drops of alcohol are added, and the benzoic acid is extracted by means of 60 c.c. of benzene in a suitable extraction apparatus. After five hours, the benzene is washed twice with 5 c.c. of cold water to remove other acid substances, and then titrated with *N*/10- or *N*/50-alkali, using phenolphthalein as indicator. After adding a few more

c.c. of alkali, water is added, and, after shaking, the alkaline layer is drawn off. The solution is then acidified with a few c.c. of dilute sulphuric acid, and the benzoic acid extracted by shaking with 50 c.c. of ether; the ether is decanted into a long, narrow beaker containing 5—10 c.c. of water, and allowed to evaporate, when crystals of the acid will become visible on the sides of the beaker. A few drops of the aqueous liquid are then tested for the possible presence of salicylic acid by means of a drop of 1% ferric chloride. If this is absent, the presence of benzoic acid may be confirmed by warming for ten minutes with 2 c.c. of 0·5% hydrogen peroxide, and, after cooling, testing with ferric chloride, which will then give the characteristic violet colour. If salicylic acid is present, the process is modified as follows:

The benzene solution is titrated for the joint acids, then rendered alkaline, and the aqueous layer is separated from the benzene.

After carefully neutralising with $N/10$-sulphuric acid, the solution is made up to 100 c.c., and in an aliquot part the salicylic acid is estimated colorimetrically by means of ferric chloride.

If by way of a check it is desired to estimate the benzoic acid directly, it may be isolated in a pure condition by acidifying the remainder of the liquid and shaking with ether. On evaporating the ether, the residue may be freed from salicylic acid by warming with a slight excess of alkaline permanganate, which does not affect the benzoic acid. After removing the excess of permanganate by means of sulphurous acid, the benzoic acid may be recovered from the acidified liquid by extraction with benzene, and then be again titrated. If "saccharin" is also present, the method becomes more complicated, and steam distillation must be resorted to. L. de K.

Estimation of Salicylic Acid by Distillation of its Dilute Aqueous Solutions. Noel C. Cassal (*Chem. News*, 1910, **101**, 289).—The estimation of salicylic acid in such liquids as wine, etc., by extraction with a solvent is often vitiated by the simultaneous extraction of other substances; further, when an attempt is made to separate the salicylic acid by distillation, very variable results are obtained, owing to the fact that many organic substances have an inhibitory effect on the distillation of the acid. The author therefore recommends the following process, which is a combination of the extraction and distillation methods. The salicylic acid is first extracted from the wine by means of chloroform, and the chloroform solution is then shaken several times in succession with dilute alkali solution in order to obtain the salicylic acid in aqueous solution. The alkaline solution is acidified with phosphoric acid and distilled, the salicylic acid passing over into the distillate being estimated colorimetrically. When 90 per cent. of the solution is distilled, from one-fifth to one-sixth of the salicylic acid present is found in the distillate; the quantity found is therefore multiplied by the factor 5·5 to obtain the amount present originally. W. P. S.

Determination of Aldehydes in Distilled Liquors. Mariano Vivencio del Rosario (*Philippine J. Sci.*, 1910, **5**, 29—32).—The process is a modification of Ripper's method. Twenty-five c.c. of the alde-

hyde solution, which must contain about 0·5% of the aldehyde, are mixed with 50 c.c. of 4% potassium hydrogen sulphite in an Erlenmeyer flask, which is stoppered and set aside for fifteen minutes, being occasionally shaken. Meanwhile, 50 c.c. of the sulphite solution are titrated by $N/10$-iodine and starch paste. At the expiration of the fifteen minutes, the mixture is also titrated. The difference between the two titres is a measure of the bisulphite combined with the aldehyde. The amount of aldehyde is given by the expression nM/20,000, where M is the molecular weight of the aldehyde, and n is the number of c.c. of $N/10$-iodine used. C. S.

Detection of Hexamethylenetetramine in Musts and Wines. BONIS (*Ann. Falsif.*, 1910, **3**, 250—253).—The test described by Voisenet (this vol., ii, 466) was found to be quite trustworthy; as small traces of formaldehyde may be found in the distillate from wine which has not been treated with hexamethylenetetramine (these traces being formed when an acid, saccharine liquid, such as wine, is heated), it is doubtful whether there is any practical advantage in using a test as sensitive as the one in question; erroneous conclusions may be formed should a mere trace of formaldehyde be detected. The usual magenta-sulphurous acid reagent is sufficiently sensitive for all ordinary purposes, and the coloration it yields is characteristic of formaldehyde if the test be applied in sulphuric acid solution. W. P. S.

The Influence of Urea on the Estimation of Amino-acids by Formaldehyde. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, **67**, 105—114).—The explanation given by Henriques and Sörensen why the formaldehyde method gives too low results in mixtures of ammonia and amino-acids is correct. It does not, however, appear necessary that methyleneimine should be first present, for probably ammonia and ammonium compounds have the same action. Other amino-compounds are also able to effect an exchange of NH_2 for OH. The addition of urea inhibits the opposing action of ammonia compounds and amino-acids. The practical outcome is that in urine, the method gives correct results. W. D. H.

Analysis of Ferrocyanides. HAROLD G. COLMAN (*Analyst*, 1910, **35**, 295—301).—A reply to Skirrow (this vol., ii, 361). The Feld magnesium chloride process as used by the author (*ibid.*, 1908, **33**, 261) has again proved to be very satisfactory. L. DE K.

The Iodometric Estimation of Potassium Ferro- and Ferricyanide. WERNER MECKLENBURG (*Zeitsch. anorg. Chem.*, 1910, **67**, 322—338).—Potassium ferricyanide may be estimated by the iodometric method, according to the equation $K_3Fe(CN)_6 + KI = K_4Fe(CN)_6 + I$, in the presence of a zinc salt. The salt to be analysed (0·5—1·5 gram) is dissolved in 500—750 c.c. of water, and 10—15 c.c. of concentrated hydrochloric acid are added. The addition of 10—15 grams of potassium chloride renders the precipitate less colloidal. After adding 10—20 c.c. of a 10% solution of potassium iodide and 10 c.c. of a $N/1$-solution of zinc sulphate, the liquid and precipitate are allowed to

remain for three minutes in a stoppered flask, starch solution is then added, and nearly a sufficient quantity of $N/10$-sodium thiosulphate. After three minutes the titration is completed. The results are slightly (0·1%) too low, owing to adsorption by the precipitate. Similar results are obtained in acetic acid solution.

Potassium ferrocyanide may be estimated in the same way if previously oxidised. The solution in hydrochloric acid, as above, is oxidised with approximately $N/10$-permanganate solution, the excess being removed by oxalic acid. The estimation then proceeds in the usual way.

Potassium ferrocyanide may be estimated directly by the following method. The salt is dissolved in 600—800 c.c. of water and 10—15 c.c. of concentrated hydrochloric acid; a concentrated solution of 15—20 grams of sodium acetate is then added, and $N/10$-potassium permanganate solution is run in until the red colour persists. Ten c.c. of 10% potassium iodide solution are added, followed by starch, and, after three minutes, the iodine is titrated with $N/10$-sodium thiosulphate. Acetic acid usually contains reducing substances, and should not be used.

Pure potassium ferrocyanide is prepared by dissolving repeatedly in water and precipitating with alcohol.

When both ferricyanide and ferrocyanide are present, sodium acetate is added to the hydrochloric acid solution, and the ferrocyanide is estimated by the permanganate method. Hydrochloric acid, potassium iodide, and zinc sulphate are then added, and the total ferricyanide is estimated as described above. C. H. D.

Strzyzowski's "Double Ureometer." O. VON SPINDLER (*Chem. Zentr.*, 1910, 1, 1549—1550; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 91—93).—The author duplicates his apparatus and carries out an estimation with a known quantity of urea (2—5 c.c. of a 1% solution) simultaneously with the estimation proper. In this way the necessity is obviated for the temperature and pressure corrections and for allowance for undecomposed urea. The nitrogen is collected in graduated tubes immersed in water, both tubes being in the same water vessel. E. J. R.

The Estimation of Ammonia and Urea in Blood. CHARLES G. L. WOLF and MCKIM MARRIOT (*Biochem. Zeitsch.*, 1910, **26**, 165—170).—The ammonia and urea were estimated in the same portion of the blood. After defibrination and filtration, 50 c.c. of saturated sodium chloride solution were added to 100 c.c. of blood, and to this mixture were added, with constant stirring, 250 c.c. of methyl alcohol. The liquid was then filtered off from the precipitate through a Löben pressure filter, and the filtrate placed for some time in an ice-chest and then filtered from the small deposit which settled. In 100 c.c. of this filtrate, the ammonia was estimated by the addition of 10 c.c. of $2N$-sodium carbonate solution, and evaporation in a vacuum, the ammonia thus set free being collected in Drechsel flasks containing $N/50$-sulphuric acid. The amount thus obtained could then be estimated by titration. In the residual liquid which was not

evaporated off, the urea could be estimated by either the Folin magnesium chloride method, or the Pflüger-Schöndorf phosphoric acid method. The ammonia estimations gave satisfactory results, whereas the urea estimations were not quite so concordant. S. B. S.

A Reagent for the Biuret Test. WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, lx).—The reagent recommended consists of a 1% solution of potassium hydroxide, treated with sufficient 3% copper sulphate to impart a slight blue colour to the solution. All the required copper is held in solution.

W. D. H.

Estimation of Caffeine in Kola. DESVIGNES (*J. Pharm. Chim.*, 1910, [vii], **2**, 20—22).—Fifteen grams of the dried Kola powder are mixed with 10 grams of magnesium oxide, and enough water is then slowly added to get a semi-liquid paste. The whole is left in a warm place, with occasional stirring, until the mass has become perfectly dry. It is then placed in a percolator and moistened with 30 c.c. of chloroform. After three or four hours, the chloroform is drawn off and the mass exhausted by percolating six times in succession with 20 c.c. of chloroform. The chloroform is then allowed to evaporate in a tared dish or recovered by distillation, and the caffeine is dried in the water-oven and weighed; it should be quite white. L. DE K.

Detection of Morphine in Organs. GUNNER JÖRGENSEN (*Zeitsch. anal. Chem.*, 1910, **49**, 484—486).—In the usual process for the detection of morphine, the acid liquid is first shaken with pure ether (or other solvent) to remove impurities, and, after rendering alkaline, the alkaloid is extracted with hot amyl alcohol, ethyl acetate, or chloroform containing alcohol.

The author, however, prefers using, instead of these solvents, ether containing 1 to 1·5% of alcohol; as morphine is but sparingly soluble therein, the extraction should be repeated ten times, but a very pure alkaloid is obtained. If highly coloured liquids have to be extracted, it is better to use amyl alcohol first; the solution is then shaken with acidified water, and from this the morphine is recovered by the ether-alcohol mixture as directed. L. DE K.

Estimation of Morphine in Cases of Poisoning. CHARLES R. SANGER and WILLIS A. BOUGHTON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, xxxvii—xxxix).—Kobert's test may be made approximately quantitative. The morphine residue is treated with a few drops of a dilute solution of formaldehyde in sulphuric acid; after a time the blue residue is diluted, neutralised with sodium hydroxide, and the resulting brown solution is made up to a definite volume in a Nessler tube. Comparison standards are made by treating known amounts of morphine in the same way. W. D. H.

Analysis of Proteins. THOMAS B. OSBORNE and D. BREESE JONES (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, **7**, viii—ix). —Loss may result from incomplete hydrolysis, formation of humin,

incomplete separation of glutamic acid, and incomplete esterification. Analysis of a mixture of pure amino-acids in the same proportion as they were obtained from zein showed that a loss of from 28 to 57% may occur. W. D. H.

Estimation of Peptide Compounds in Proteins and in Their Cleavage Products. VALDEMAR HENRIQUES and J. K. GJALDBAK (*Zeitsch. physiol. Chem.*, 1910, 67, 8—27).—Experiments have shown that when Witt's peptone is evaporated twice to dryness on the water-bath there is still some nitrogen present as peptide nitrogen (some 19·2% of the total originally present).

Complete hydrolysis can be brought about by boiling with 20% hydrochloric acid for twelve hours.

The same holds good for many other proteins, but in the case of egg-albumin the hydrolysis is not complete even after twelve hours' boiling with concentrated hydrochloric acid. With substances which are readily hydrolysed, or which have previously undergone prolonged hydrolysis with enzymes, six hours' boiling is sufficient to complete the hydrolysis. Complete hydrolysis can also be brought about by heating at 150° for 1·5 hours, or at 120° for three hours, in sealed tubes with 3*N*-hydrochloric acid. Sulphuric acid is not so efficient.

In all cases the total nitrogen present as amino-acids and as ammonia was estimated by Sörensen's formaldehyde titration method, the ammonia then estimated by distillation under reduced pressure with methyl alcohol and barium hydroxide, and the amino-acids by difference. The process of heating with hydrochloric acid at 150° or 180° tends to increase the amount of ammonia nitrogen beyond the value obtained by merely boiling with hydrochloric acid. Temperatures above 150° should not be used, as under such conditions the amino-acids are liable to undergo secondary decompositions.

Attention is called to the fact that Abderhalden had drawn the conclusion that proteins can be completely hydrolysed by contact with trypsin and erepsin for several months.

The authors' experiments show that this is not so, and that the products still contain peptide compounds. J. J. S.

The Use of Invertase in the Determination of the Alkalinity or Acidity of Biological Fluids. C. S. HUDSON and WILLIAM SALANT (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xiii).—Yeast invertase loses on dialysis its acid and most of its activity; the latter returns on the addition of acid. If its activity in water is taken as 300, in various bloods this is lowered to figures varying from 266 (dog's blood) to 69 (pig's blood). If blood is dialysed, it loses the power of lowering the activity of invertase, showing that the lowering is due to salts. W. D. H.

General and Physical Chemistry.

The Relative Duration of the Rays of Calcium in the Spark with Self-Induction. GUSTAVE A. HEMSALECH (*Compt. rend.*, 1910, **151**, 220—223).—By the use of a method previously described (*Compt. rend.*, 1905, **141**, 1227; 1910, **150**, 1743), the relative duration of the calcium rays has been measured. For the "arc" rays the time of duration is, as in the case of iron, nearly proportional to their intensity, and varies between 93 and 233 microseconds. The coefficient of augmentation produced by increasing the capacity from 0·0023 to 0·012 microfarad was nearly the same (1·4 to 1·5) for all rays except the strongest, 4227, for which it was 1·25. The duration of the "spark" rays was shorter, considering their intensity, than the "arc" rays, the most brilliant of all having shorter duration than many of the "arc" rays. For the impurities, strontium and aluminium, the duration of certain rays was also determined, and as these sometimes differ from the rays of the pure substance, useful indications may in certain cases result from the method in analysing a substance containing unknown impurities. F. S.

Phosphorescence. GEORGES URBAIN (*Bull. Soc. chim.*, 1910, [iv], **7**, i—xiii).—A lecture delivered before the French Chemical Society. E. H.

A Photographic Method of Recording α-Particles. WILLIAM DUANE (*Compt. rend.*, 1910, **151**, 228—230 *).—In the method described, the image of a gold-leaf of a sensitive electroscope is thrown by means of a Nernst lamp and lens on a slit, behind which a Kodak film is moved transversely to the slit by clockwork. The connecting wire to the electroscope passes through an ionisation chamber containing polonium (which discharges it after each charge) to the electrode of a small ebonite box of less than 1 c.c. volume, into which α-particles enter through a small hole in the bottom covered with thin mica, and which is exhausted to 1 or 2 cm. pressure. The bottom of the box is of metal connected to a high tension battery of accumulators, the potential being arranged so that a spark just does not pass. By this modification of Rutherford and Geiger's apparatus, a photographic record of the sudden movements of the gold-leaf produced by the individual α-particles is obtained. Specimen portions of the film with and without a source of α-particles show the effect of the latter with great clearness. F. S.

The β-Activity of Uraninite. STEWART J. LLOYD (*J. Physical Chem.*, 1910, **14**, 509—527).—The percentage β-activity contributed by the β-ray constituents of uraninite has been found to be:

Uranium-*X*	32·1	Total 95 2%.
Radium-*B*	16·1	
Radium-*C*	36·1	
Radium-*E*	10·9	

* and *Le Radium*, 1910, **8**, 196—198.

The electroscope employed was a cylinder 40 cm. high and 40 cm. diameter. The β-activity of the powdered uraninite was corrected for absorption in the substance by extrapolating the curves of activity, obtained with increasing thickness of films, back to the origin, and for loss of emanation from the powdered uraninite which was measured.

The proportions due to uranium-*X* and radium-*B* and -*C* were obtained by comparing the β-activities of these substances obtained from known quantities of uranium and radium. Many observations on the separation of uranium-*X* from uranium and impurities are described. Stirring soot, obtained freshly from the burning of naphthalene, into acetone solution of uranyl nitrate, extracting the soot with hydrochloric acid, adding iron, and precipitating the iron and uranium-*X* with excess of ammonium carbonate, gives good results. The only way of freeing ammonium-*X* from iron is to dissolve in concentrated hydrochloric acid, and to extract with freshly distilled ether saturated with hydrogen chloride, when the uranium-*X* is left in the aqueous solution. In the electroscope employed, 26·7% of the total ionisation due to uranium-*X* was contributed by the soft β-rays, and these are *not* included in the foregoing table. The existence of radio-uranium is questioned. Measurements of the active deposit produced by the emanation of a known quantity of radium gave the proportion of β-rays due to radium-*B* and -*C* together, that due to the latter alone being determined by volatilising the former at 700°. The radio-lead was chemically separated from uraninite with added lead, and left to accumulate the equilibrium amount of radium-*E*, which was then separated from the lead solution by adding a drop of iron and sodium hydroxide in excess, when the radium-*E* remains undissolved with the iron. The β-rays of uraninite, in the electroscope used, gave an ionisation equal to the α-rays of 23·5 sq. cm. of a thick film of U_3O_8.

F. S.

The Experimental Testing of the Question of the Nature of the γ-Rays. II. EGON R. VON SCHWEIDLER (*Physikal. Zeitsch.*, 1910, **11**, 614—619. Compare this vol., ii, 376).—In a further purely theoretical discussion of the nature of the variations in the intensity of γ-rays from instant to instant to be expected on the various "corpuscular" and "impulse" theories, various criticisms of the first paper, resulting from a correspondence with Sommerfeld, Planck, Bragg, and Campbell, are taken into account, and these modify the earlier conclusions. The most important refer to the possibility that, in addition to the other probability variations, the number of pairs of ions produced by the individual γ-ray in the gas may vary (Campbell), and to the established fact that the γ-ray ionisation is largely, if not wholly, due to the soft secondary radiation and not to the primary radiation directly (Bragg). The various hypotheses are reviewed in detail, and the nature of the variations theoretically to be expected in each case worked out. The conclusion is drawn that an experimental means of testing the two theories is not possible if the γ-ray ionisation is produced by secondary rays, although the absolute magnitude of the variations of ionisation is within the limit of experimental detection whichever theory is correct.

F. S.

The Helium in Recent Minerals. ARNALDO PIUTTI (*Le Radium*, 1910, 7, 178—179).—Other investigators previously have not detected helium in the strongly radioactive minerals carnotite, torbernite, and autunite (compare Bordas, Abstr., 1908, ii, 505).

With the apparatus described in a previous paper (*Le Radium*, 1910, 7, 142), the spectrum of helium was clearly detected in the two first, but not in the last, quantities of 3 grams being employed. The limit of detection is given as 0·036 cu. mm. of helium. In the very interesting cases of minerals, which are strongly radioactive, formed in contemporaneous eruptions of Vesuvius, the presence of helium could not be detected. The activity of the minerals formed in the eruption of 1906 (cotunnite and galena) has been shown to be due to radium-*D*, -*E*, and -*F* only, and it is reasonable to draw the conclusion that sufficient time has not elapsed for a detectable quantity to have accumulated. In galena from the more ancient lava of Monte Somma, neither helium nor radioactivity could be detected, nor in titanite (0·32 gram) from Ischia, which was radioactive. F. S.

The Density of the Radium Emanation. SIR WILLIAM RAMSAY and ROBERT WHYTLAW GRAY (*Compt. rend.*, 1910, 151, 126—128).—The volume of the emanation used has been calculated from the value previously found for the volume in equilibrium with 1 gram of radium (0·601 cu. mm.), and in no case exceeded 0·1 cu. mm. This was weighed sealed up in a small capillary tube on a quartz balance of which the sensitiveness exceeds the half-millionth of a milligram (compare Steele and Grant, Abstr., 1909, ii, 876), in which the pressure of the air in the balance case was adjusted, and the buoyancy of a small sealed quartz bulb containing air used instead of weights. The tip of the capillary was then broken, and its weight again taken. Five measurements of the density are given, in which the weight of the emanation found was of the order of 6×10^{-7} gram, and values for the molecular weight between 216 and 228 were obtained. The mean value was 220. There is now therefore no doubt that the true atomic weight is 222·5, as deduced from the disintegration theory by subtracting from the atomic weight of radium 226·5, the weight of the atom of helium 4 expelled as an α-particle. To put the radium emanation in its proper place as the second member in the series of inactive gases after xenon, the name *Niton*, symbol Ni, is proposed.
F. S.

The Slow Precipitation of Radium Sulphate. LÉON KOLOWRAT (*Le Radium*, 1910, 7, 157—159).—A series of experiments has been made with a dilute solution of pure radium chloride after addition of sulphuric acid and filtration, to investigate the slow continuous diminution in the rate of production of emanation in the solution observed by Mme. Curie. It was found that after some weeks, when the rate of production had fallen to about one-half the initial value, heating to 70° before the test increased the amount of emanation evolved enormously. Heating and removal of the emanation before the time of accumulation for the test resulted in a nearly normal result. In a series of tests in which the temperature at

the test was lower than at the preceding test, the quantity of emanation steadily diminished. The results obtained agree quantitatively with the view that an invisible precipitate of radium sulphate slowly forms in the solution, and from this precipitate the emanation is not all liberated, but accumulates. On heating the emanation is obtained, not only from the solution, which is formed during the period of accumulation between the tests, but also from that part of the precipitate, soluble at the higher, but insoluble at the lower temperature, which has been accumulating since the precipitate was formed. There is therefore no necessity for supposing that a new member exists, intermediate in the series between radium and its emanation (radium-*X*). A perfect analogy exists between the phenomena observed in solutions and in solids (Kolowrat, this vol., ii, 91).

F. S.

The Constituents of the Induced Activity of Actinium. Mlle. L. BLANQUIES (*Compt rend.*, 1910, **151**, 57—60; *Le Radium*, 1910, **7**, 159—162. Compare Abstr., 1909, ii, 634).—Further experiments are described to test the view that the α-rays of actinium-*B* are complex and derived from two consecutive changes. The supposed product of actinium-*B* is termed actinium-*B'*. The active deposit of actinium electrolysed in hydrochloric acid solution gave on the cathode a product decaying rather more rapidly during the first minute than would be the case if it consisted of actinium-*B*. The effects observed were small, but a period of about 2·25 minutes is attributed to the new substance. The recoil product from the active deposit consists mainly of actinium-*C* with some actinium-*A*. It decays at first rather more rapidly than the latter, which may be due either to actinium-*B'* recoiling from actinium-*B*, or to the latter removed mechanically like actinium-*A*, so this evidence is equivocal. The scintillations produced by the active deposit placed at a fixed distance from the zinc sulphide screen, the pressure of the gas in the apparatus being varied, were compared with those produced by polonium.

At a pressure 1 cm. below that which caused the scintillations to disappear, increase of pressure caused between two and three times more rapid diminution of the number of scintillations in the case of actinium than in that of polonium. This is well in agreement with what is to be expected on the view under consideration. The analogy between actinium and thorium, and the large proportion of double scintillations observed with the active deposit of actinium (compare Geiger and Marsden, this vol., ii, 92), also supports the view, although it has not been possible to obtain as yet any complete proof of its correctness. F. S.

Radioactivity of the Mineral Springs of Switzerland. Emanation Content of the Water. II. ALFRED SCHWEITZER (*Arch. Sci. phys. nat.*, 1910, [iv], **30**, 46—66. Compare Abstr., 1909, ii, 363).—The previous investigations have been continued on many new springs with improved apparatus, designed for use with hot waters, in which the latter are contained during measurement in an

hermetically closed vessel. Three new springs containing notable quantities of emanation have been found. One in the Val Lumpegnia, near Disentis, had an activity of 9·16 Mache units. The other two were Spring No. 2 of Gränichen (7·56), and the "Satro" spring at Acquarossa (5·17). F. S.

The Exclusive Presence in Gases Derived from Certain Hydrogen Flames of Ions Completely Analogous (in Mobility) to those Produced by Röntgen Rays. MAURICE DE BROGLIE (*Compt. rend.*, 1910, **151**, 67—68. Compare *ibid.*, **150**, 1425).—With proper precautions, numerous hydrogen flames produce only small ions, which previously had been observed only for the carbon monoxide flame. The combustible gas, well filtered and dried, is diluted with nitrogen and burnt with a very small flame at the foot of a lead tube inside a very dry tube carefully cooled with cold water. The flames employed consisted mainly of hydrogen, ethyl ether, acetaldehyde, acetone, and pentane, whilst illuminating gas continued in these circumstance still to give ions of feeble mobility. The mobility of the small ions was between 0·75 and 1 in terms of that of those given in ordinary circumstances by *X*-rays or radium. The results indicate that chemical action and high temperature together produce small ions, which in absence of precautions are transformed into large ions by condensation, solid walls in the neighbourhood of the flame as well as water vapour being necessary. The results explain those of von Helmholtz on the efficacy of different flames to condense a steam jet, the ether flame producing scarcely any effect, and even being cited as not giving ionisation. This is due to the small ions being far less active in promoting condensation than the large ions, and to their rapid recombination rendering the conductivity of the gas more ephemeral. F. S.

Conduction of Electricity in Mixtures of Metals and their Salts. II and III. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1910, **73**, 578—597, 624—637. Compare Abstr., 1909, ii, 537).—II. The electrical conductivity of fused mixtures of cadmium and cadmium chloride at 580°, 600°, and 620° has been determined by the method already described (*loc. cit.*). The conductivity of the mixtures increases rapidly as the temperature is raised, whilst the addition of cadmium to fused cadmium chloride progressively lowers the specific conductivity.

This lowering may be due to the absence of any passage of electrons from metal to solution or to the very small velocity of the electrons in the mixture; in the first case the dissolved metal should have no conductivity, and in the latter case its conductivity should be of the same order as that of an electrolyte. In connexion with this point, the density of the mixtures of cadmium chloride and metal has been determined at 600°. The density of the chloride at this temperature is 5·299. The available data show that the conductivity of the dissolved metal is very small, much smaller than that of the chloride, and it may be zero; they do not, however, serve to decide conclusively between the two views as to the effect of the metal.

Freezing-point determinations with mixtures of cadmium chloride and cadmium appear to show that no compound of the formula CdCl separates from the fused mass, and this view is supported by microscopic observations. The compound CdCl may, however, exist in the fused mixture.

III. Equations are deduced which show the influence of different factors on the validity of Faraday's law for the electrolysis of a mixture of cadmium chloride saturated with metallic cadmium. It is shown that if the mixture has no metallic conductivity and no complex formation takes place, more metal will pass into solution that corresponds with Faraday's law. This deviation will be increased if complex formation between $CdCl_2$ molecules and anions or electrons occurs, and also if the dissolved metal is partly present in the form of a subchloride.

Experiment shows that for 1 equivalent of silver, 0·83 equivalent of cadmium is dissolved or set free, so that either metallic conductivity or complex formation, or both, must occur. Although the data are not sufficient to decide the question conclusively, the deviation from Faraday's law appears too great to be accounted for by metallic conductivity alone. G. S.

Reactions in the Iron–Nickel Peroxide Accumulator. III. Behaviour of the Iron Electrode. FRITZ FOERSTER and VIKTOR HEROLD (*Zeitsch. Elektrochem.*, 1910, **16**, 461—498).—The study of the nickel peroxide electrode (Abstr., 1908, ii, 146, 147, 558) is now completed by a very exhaustive investigation of the iron electrode. Faust (Abstr., 1907, ii, 426) found that the iron electrode is discharged in two (possibly three) stages. The authors have studied these both analytically and electrically. The potentials of the iron electrode are referred to the normal hydrogen electrode, compared with which the iron is negative. Faust used zinc in 20% potassium hydroxide as a standard electrode; its potential compared with the hydrogen electrode is $-1·27$ volt, which makes it possible to compare Faust's measurements with those in the present paper.

The electrodes were made by pressing a mixture of finely divided iron and graphite into the perforated steel cells used by Edison in his accumulator. An impalpable iron powder is obtained by Edison's process by reducing a fine-grained ferric oxide with hydrogen at about 480°, and then drowning it in water, by which treatment it loses its pyrophoric properties owing to a surface oxidation. A more coarse-grained powder was also used. The metallic iron is these powders is estimated by boiling with mercuric chloride, which dissolves the metal, but has no action on ferrous or ferric oxide.

When an electrode is first made, the iron is passive (2·85*N*-potassium hydroxide solution is the electrolyte used throughout the experiments), but a very small quantity of occluded hydrogen is sufficient to make it active. This hydrogen charge may be given to the iron either by cathodic polarisation or by treatment with an acid or a neutral solution of ferrous sulphate. The potential of the electrode (at 18°) is $-0·87$ to $-0·88$ volt, and during the first stage of the discharge it remains near this value. The chemical change which occurs is the

conversion of iron into ferrous hydroxide. The ferrous hydroxide forms a film round each particle of iron, which prevents its contact with the electrolyte; the charge of hydrogen is therefore soon oxidised and cannot be replaced by the interaction of electrolyte and iron, and the latter becomes passive. The second stage now sets in, the chemical reaction supplying the current being the oxidation of ferrous to ferric hydroxide. The potential of an electrode consisting of graphite and ferrous hydroxide is -0.74 to -0.76 volt, which is also the potential of the iron electrode in the second stage of the discharge. During this stage, iron reacts with the ferric hydroxide, forming ferrous hydroxide, so that the analyses of the electrode show that iron disappears and ferric hydroxide is formed. The effect of adding mercury to the iron powder (in the recent forms of the Edison accumulator) is studied. The effect is to increase the capacity of the first stage by keeping the iron in the active state longer than is the case without mercury. In charging the electrode, the ferric hydroxide is reduced quantitatively, but the ferrous hydroxide is only reduced slowly, so that a large quantity of hydrogen is evolved and the efficiency of the electrode is far from theoretical. Since the oxidation of the iron in discharging the electrode is only superficial, it is necessary, in order to get considerable capacity, to use the iron in the most finely divided form that can be obtained. T. E.

The Rectilinear Diameter for Oxygen. ÉMILE MATHIAS and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, **151**, 213—216. Compare Abstr., 1909, ii, 552).—A discussion of the surface representing the state of gases at the critical temperature, with an account of the method employed in the case of oxygen to determine whether the diametral line is rectilinear for a gas having a very low critical temperature. W. O. W.

Absorption of Gases by Charcoal. IDA F. HOMFRAY (*Proc. Roy. Soc.*, 1910, **84**, *A*, 99—106 *).—The apparatus employed was of the nature of a gas thermometer; the bulb contained 3 grams of charcoal, and the equilibrium pressures exerted at different temperatures after the admission of successive volumes of a gas were measured. Experiments were made with helium, argon, nitrogen, carbon monoxide, methane, ethylene, carbon dioxide, and oxygen, as well as with mixtures of carbon monoxide and nitrogen, and the temperatures of observation extended from that of liquid air to the boiling point of aniline.

The measurements were first represented on isothermal and isobaric diagrams, and from these, points of equal absorption were read off and curves, so-called "isosteres," plotted, having pressures as ordinates, and absolute temperatures as abscissæ. The concentration by weight, C, for each isostere is calculated in the form $C = 100w/(W+w)$, where $w =$ weight of gas absorbed in W grams of charcoal.

The following two relationships have been found to hold: (1) at constant concentration $T'_0/T_1 - T'_0/T'_1 = R(T_0 - T'_0)$, where T_1 and T'_1 are the absolute temperatures read from any one isostere at any two pressures, T_0, T'_0 are the absolute temperatures at which any saturated vapour

* and *Zeitsch. physikal. Chem.*, 1910, **74**, 129—201.

taken as standard has the same pressures, and R is a constant; (2) at constant pressure: $-dT/(d \log C) = K$. From these two relations, if the vapour-pressure curve of a liquefied gas is known, together with three values of temperature, pressure, and concentration in the presence of charcoal, the whole absorption diagram can be mapped. The values of $dT/(d \log C)$ for the different gases at the same pressure increase uniformly with increasing complexity of molecular structure from argon to ethylene.

From the isosteric curves, the molecular heat of absorption, λ, can be calculated by the thermodynamical formula: $\lambda = 2T^2.d \log_e P/dT$. A simple method of calculating the results is described, and the applicability of the formula has been shown by direct calorimetric measurements with carbon dioxide at atmospheric temperature.

The absorption curve for mixtures of nitrogen and carbon monoxide is found to lie between those for the single gases at all compositions. From this result, certain deductions are made which may be of value in separating mixed gases by selective absorption in charcoal.

The nature of absorption is discussed. Objections are advanced to explanations on the basis of chemical combination or surface condensation, and a solution hypothesis is favoured. The fundamental objection to the latter explanation is that Henry's law does not hold for the distribution between gas space and charcoal, but in the present case the solutions are by no means dilute, and the deviations from the simple laws appear to be analogous to those shown by concentrated solutions. G. S.

Adsorption of Iodine by Solids. MARCEL GUICHARD (*Compt. rend.*, 1910, **151**, 236—238. Compare Abstr., 1909, ii, 136).—Attention has previously been called to the persistence with which iodic anhydride retains iodine. A table is now given, showing for silica and the oxides of aluminium, magnesium, and glucinum in different physical states the amount of iodine adsorbed and the length of time required for saturation. Oxides prepared by calcination at a high temperature, and having a density approaching the limit, take up only traces of iodine. Carbon heated at 600° adsorbs 34·2% at the ordinary temperature. W. O. W.

Dimorphism and Mixed Crystals occurring in Liquid-Crystalline Substances. Applications of the Phase Rule. OTTO LEHMANN (*Zeitsch. physikal. Chem.*, 1910, **73**, 598—623).—Largely polemical against Prins (compare Abstr., 1909, ii, 869) and Schenck (*Krystallinische Flüssigkeiten*, Leipzig, 1905, etc.), and is partly concerned with questions of priority. With reference to some of the points in dispute, the transition and saturation temperatures for mixtures of cholesteryl decoate and *p*-azoxyanisole have been determined by means of the author's crystallisation-microscope, and the results are figured and described in detail. G. S.

Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1910, **73**, 547—556. Compare Abstr., 1909, ii, 277, 561, 723).—The number

of visible particles in a definite volume of a colloidal solution observed under the ultramicroscope varies, owing to Brownian motion. If n is the momentary value observed, n_1 the number of gas-molecules which would be present in this volume if the distribution were uniform, and $\bar{\delta} = (n - n_1/n_1)$ is the mean deviation when all the positive and negative deviations are taken into account, then, as shown by von Smoluchowski (*Ann. Physik*, 1908, [iv], **25**, 205), $\bar{\delta} = \sqrt{2/n_1\pi}$ if n_1 is a large number, and $\bar{\delta} = 2n_1^k.e^{-n_1}/k!$ when n_1 is a small number, provided that the gas laws are valid for the solution. In the last formula, k is the greatest whole number less than or equal to n_1. If the gas laws do not apply, then $\bar{\delta} = \sqrt{2/n_1\pi}\sqrt{\beta/\beta_0}$ when n_1 is a large number (β is the actual compressibility, and β_0 the compressibility, provided the gas laws hold). If n_1 is a small number, then $\bar{\delta} = (2n_1^k.e^{-n_1}\sqrt{\beta/\beta_0})/k!$ approximately.

The author has counted the particles in a limited volume of solution of colloidal gold and in one of colloidal mercury under the ultramicroscope, and finds on applying the above formulæ that the gas laws apply to dilute solutions, but the observed osmotic pressures are greater than the theoretical values in relatively concentrated solutions.

G. S.

Some Presumed Chemical and Physical Effects of Pressure Uniform in all Directions. GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1910, **45**, 525—538).—If fine filings of copper or silver are enclosed in a steel cylinder under a pressure of 8000 atmospheres for a month at the ordinary temperature, apparently homogeneous cylinders are obtained, as described by Spring. Microscopical examination shows, however, that the filings are still distinct, and are merely united by adhesion, no molecular interpenetration having taken place. Similarly, a mixture of copper and silver filings yields a cylinder in which the original silver and copper particles are clearly distinguishable. It is improbable that the diffusion would take place if longer time were allowed, as a microscopical examination of the native copper of Keveenaw Point, in which inclusions of silver occur, shows that diffusion has not occurred to any measurable extent during a geological epoch.

Experiments with lead and wax under a pressure of 9,900 atmospheres at 15°, continued for twelve days, show that the lead does not behave as a fluid under such conditions. There is thus a complete difference between the effects of pressure uniform in all directions and of pressure causing flow through an orifice, and there is no reason to assume that pressure of the former type produces any plasticity or increases diffusion. There is no tendency for a cylinder or prism, subjected to pressure uniform in all directions, to assume a spherical form. In the experiments of Spring and Kahlbaum, the diminution of density observed under high pressures is to be attributed to inequalities in the distribution of pressure, producing deformation.

C. H. D.

Periodicity of the Properties of the Elements. New Arrangement. JAMES F. TOCHER (*Pharm. J.*, 1910, [iv], 31, 159—160).—The

elements are arranged in a logarithmic spiral. The radius vector, r, in three-dimensional space, is a function of the atomic weight and of the atomic volume of each element. The vectorial angle is a function of the valency of an element; it has a constant value, $\theta = \pi/8$, and in the spiral is the angle between two adjacent radii, one with an element E_n and the other with an element E_{n+1} with next higher atomic weight.

The figure of a model is given, in which the atomic weight of each element is shown as a length on the xy plane, and the atomic volume as a height on the xz plane. If valency is defined as the combining power of an element with hydrogen, the valency varies as sin θ, being zero along the x axis, on which lie the inert gases, and attaining a maximum at 90° and at 270°. The first or upper right-hand quadrant contains the electro-negative elements, the heavy and the noble metals are situated mainly in the second quadrant, the rarer elements mainly in the third quadrant, whilst the fourth quadrant contains the alkali metals and other strongly positive elements. The scheme can only be appreciated by reference to the model. C. S.

Inorganic Chemistry.

Nitrous Oxide. I. ALFRED STAVENHAGEN and E. SCHUCHARD (*Ber.*, 1910, **43**, 2171—2174).—When sulphur is strongly heated in a stream of nitrous oxide, it burns with a brilliant bright greenish-blue flame. If the combustion is carried out in a large glass vessel, the walls become covered with crystals of nitrosulphonic acid, and at the same time nitrogen peroxide is formed in quantity.

Thus nitrous oxide may be transformed into higher oxides of nitrogen without the use of electrical energy by simply burning sulphur in it, nitrosulphonic acid anhydride or its decomposition products being formed at the same time. T. S. P.

Acceleration of the Reduction of Quinquevalent Arsenic by Hydrogen Bromide. A Correction. MARTIN ROHMER (*Ber.*, 1910, **43**, 2262).—The method described by Jannasch and Seidel (this vol., ii, 546) for the reduction of quinquevalent arsenic by means of potassium bromide or hydrobromic acid has been known for nine years (compare Abstr., 1901, ii, 194), and during that time has often been recommended in the scientific literature and in patent specifications as a catalyst for reducing actions. T. S. P.

Percarbonates. SEBASTIAN M. TANATAR (*Ber.*, 1910, **43**, 2149—2151).—The author confirms Riesenfeld's observations (this vol., ii, 290) that in solutions of the same alkalinity potassium percarbonate liberates more iodine from potassium iodide than does sodium percarbonate, but points out that this is only true when solid

potassium percarbonate is used, or a freshly-prepared solution of the same. A solution of the potassium salt which has been made for five minutes reacts similarly to sodium percarbonate. It follows that potassium percarbonate liberates iodine quicker than it undergoes hydrolysis, since as soon as hydrogen peroxide is present in the solution the iodine is decolorised.

Riesenfeld has not taken into account the fact that a solution containing 1 mol. of sodium percarbonate, ($Na_2CO_3,\frac{1}{2}H_2O_2$), contains $\frac{1}{2}$ mol. of hydrogen peroxide from the commencement, and thus the liberation of iodine is hindered.

The author considers that hitherto no reaction has been discovered which distinguishes with certainty per-salts from salts containing hydrogen peroxide of crystallisation. T. S. P.

The Ternary System: Sodium Sulphate–Sodium Fluoride–Sodium Chloride. ADOLF WOLTERS (*Jahrb. Min. Beil. Bd.*, 1910, **30**, 55—95).—The thermal and optical investigation of the systems sodium sulphate–sodium chloride and sodium sulphate–sodium fluoride has been re-investigated, as also has the system sodium chloride–sodium fluoride. None of the three components forms mixed crystals with either of the other components.

In the system sodium sulphate–sodium fluoride the compound Na_2SO_4,NaF is formed. It is enantiotropic-dimorphic, the transition temperature being 105°. Microscopical investigation showed it to be mimetic-hexagonal at the ordinary temperature, and truly hexagonal at higher temperatures. The double refraction is positive.

The refractive index of sodium fluoride for sodium light is 1·3255.

A theoretical discussion of the cooling curves and freezing-point phenomena of ternary systems is given. The ternary system sodium sulphate–sodium fluoride–sodium chloride is very simple, there being no complications, with the exception of the transformations mentioned above. The four solid phases, including the double salt, are not miscible with each other at all.

A compound corresponding with the mineral sulphohalite could be obtained neither from the fusions nor from aqueous solutions.

T. S. P.

Constitution of Sodium Hydrogen Carbonate. BIGHER (*Chem. Zeit.*, 1910, **34**, 765—766).—The author considers that the ordinary formula assigned to sodium hydrogen carbonate is incorrect, since when it is calcined with the formation of the normal carbonate the temperature is such that it cannot be supposed that the sodium atom of one molecule displaces the hydrogen atom of another molecule, the substances being in the solid state. The formula should therefore be written as $(NaHCO_3)_2$, or, better, as Na_2CO_3,H_2CO_3, a double salt of sodium carbonate and carbonic acid.

This formula is used to explain the ease with which sodium hydrogen carbonate loses carbon dioxide, and the action of ammonia, barium chloride, and lime respectively on the aqueous solutions. Equations are also given for the ammonia soda process. T. S. P.

Method for the Preparation of Stable Colloidal Metals. CESARE SERONO (*Arch. Farm. sperim.*, 1910, **9**, 152—157).—Stable colloidal solutions of certain metals may be obtained by electrolysing a solution of pure gelatin, rendered slightly conducting by an alkali chloride or sulphate, between metallic electrodes.

A 5% solution of gelatin is used, containing 1% of sodium chloride or sulphate, and contained in a glass vessel. The anode is placed in this vessel, whilst the cathode, composed of the metal to be rendered colloidal, is enclosed in an inner porous cell. A continuous current of 3 to 5 amperes is used at 120 volts. Considerable foaming takes place, and it is necessary to interrupt the operation from time to time to prevent loss of liquid. After about ten minutes, a colloidal solution of the metal is obtained in the neighbourhood of the anode. The liquid surrounding the cathode is free from metal.

In the case of gold, a violet colloidal solution is obtained containing 42 mg. of gold per litre. It is clear by transmitted, but opalescent by reflected, light, and is very stable, remaining unchanged in air for more than a month, the gold preserving the gelatin in a perfectly sterile condition. A similar colloidal solution of silver is obtained, containing 87 mg. of silver per litre. Iron yields a solution containing a ferrous salt, together with colloidal iron, and a small precipitate of ferrous hydroxide. By the prolonged action of the current, large quantities of metal may be brought into solution, in one case 3·225 grams of silver being dissolved in 448 c.c. of liquid.

It is assumed that, in the electrolysis of sodium chloride with gold electrodes, the chlorine liberated attacks the gold anode, forming gold chloride, and that the gelatin is partly decomposed, yielding acids resembling protalbic and lysalbic acids, which then reduce the gold to the colloidal metallic state, as in Paal's method of preparation.

C. H. D.

Binary Systems Formed from the Alkali Sulphates and Calcium Sulphate. HANS MÜLLER (*Jahrb. Min. Beil. Bd.*, 1910, **30**, 1—54).—The normal sulphates of potassium, rubidium, and cæsium are enantiotropic-dimorphic, being rhombic at the ordinary temperature and hexagonal at higher temperatures. Twin crystals separate from the fusions, but twinning disappears at the transition point. With rising temperature, expansion takes place at the transition point, and the cubical coefficient of expansion of the rhombic modification is greater than that of the hexagonal. The melting points are: $K_2SO_4 = 1057°$, $Rb_2SO_4 = 1051°$, $Cs_2SO_4 = 995°$, and the transition points are respectively: 580°, 649°, and 660°. The latent heat of fusion decreases very slightly from potassium sulphate to cæsium sulphate, whereas the latent heat of transition decreases very greatly in the same order, being practically zero for cæsium sulphate.

The temperature-concentration diagrams of the systems composed of calcium sulphate with potassium sulphate, rubidium sulphate, sodium sulphate, lithium sulphate, rubidium sulphate, and cæsium sulphate respectively were determined both thermally and optically, with the following results. The double salt, $K_2SO_4,2CaSO_4$, exists; it is enantio-

tropic-dimorphic, the transition temperature being 936°, and m.p. 1004°. It takes up water with the formation of a hydrate containing $\frac{1}{2}H_2O$.

Rubidium and calcium sulphates form the enantiotropic-trimorphic double salt, $Rb_2SO_4,2CaSO_4$, m. p. 1043°. The first transition point is at 915°, the second at 787°.

The double salt, $Cs_2SO_4,2CaSO_4$, was obtained from the fusions. It is dimorphic, with m. p. 959°, and a transition temperature of 722°. Pure sodium sulphate has a transition temperature at 233°, contraction taking place when the transformation takes place with rising temperature. With calcium sulphate, it forms the double salt, $4Na_2SO_4,CaSO_4$, which is completely miscible with sodium sulphate, and exists in one doubly refracting modification only. It takes up water, forming a hydrate with $1H_2O$.

Glauberite cannot be prepared by the fusion method. From a fusion having the composition of glauberite, anhydrite is first deposited, the remainder then solidifying as a eutectic of anhydride and mixed crystals of $CaSO_4,4Na_2SO_4$ with $CaSO_4$.

Lithium sulphate and calcium sulphate form neither double salts nor mixed crystals.

The double salt, Rb_2SO_4,Li_2SO_4, is enantiotropic-dimorphic; m. p. 730°, and transition temperature of 142°. The double salt, Cs_2SO_4,Li_2SO_4, exists in one modification only, m. p. 729°.

General conclusions to be drawn are as follows. It is not always possible to determine the temperature-concentration diagram by thermal methods alone, since (*a*) the heat of transformation is at times so small that the cooling curve does not show an arrest. This is the case, for example, with Cs_2SO_4 and Rb_2SO_4,Li_2SO_4. (*b*) Owing to the formation of mixed crystals, the transformation is often so retarded, or spread over so great an interval, that it is not noticeable thermally. This is the case with the system Na_2SO_4–$CaSO_4,4Na_2SO_4$. (*c*) When the fusion curve runs very close to the eutectic line only one arrest is obtained on the cooling curve; for example: the system $CaSO_4,4Na_2SO_4$–$CaSO_4$.

Optical investigations do not always lead to conclusive results, since in some cases thin sections of fusions from which one component has separated first cannot be distinguished from sections of the eutectic; in other cases, from a fusion of eutectic composition the one component may separate without, and the other with, super-cooling. The latter then appears as an older, pre-eutectic formation.

T. S. P.

Deposition of Calcium Carbonate from Solutions of Calcium Hydrogen Carbonate. F. VETTER (*Zeitch. Kryst. Min.*, 1910, **48**, 45—109).—The author has studied the deposition of calcium carbonate from solutions of calcium hydrogen carbonate in (1) pure water; (2) sea-water containing 27·90 grams of NaCl, 2·34 grams of $MgCl_2$, 1·55 grams of KCl, 0·52 gram of NaBr, 1·56 grams of $CaSO_4$, 1·85 grams of $MgSO_4$, in 1000 grams of water; (2*a*) sea-water plus 2·03 grams of ammonium sulphate per litre. Also from solutions containing in 1000 grams of water (*a*) 1·56 grams of calcium sulphate, (*b*) 27·90 grams of sodium chloride, (*c*) 1·85 grams of magnesium sulphate, (*d*) 2·34 grams of magnesium chloride, (*e*) 1·55 grams of

potassium chloride, (*f*) 20·74 grams of ammonium chloride (equivalent to 27·90 grams of sodium chloride), (*g*) 2·03 grams of ammonium sulphate (equivalent to 1·8 grams of magnesium sulphate), (*h*) a saturated solution of sodium chloride.

The solutions were saturated with calcium hydrogen carbonate under a pressure of 1 atmosphere of carbon dioxide. Eighty to 120 c.c. of these solutions were used in each experiment, and the calcium carbonate was deposited by drawing dust-free air through them for one and a-half to two hours. In some cases, nuclei of aragonite or calcite were added. The temperatures varied from 0° to 55·5°. Experiments were also made in which the deposition was brought about by first drawing air charged with ammonia through the solutions for one to two minutes, and then air alone.

In sea-water, nuclei of aragonite do not favour the deposition of that substance; in no case was aragonite alone deposited. They apparently hinder the deposition of hydrated calcium carbonate ($CaCO_3,6H_2O$), except in one case each from solutions of magnesium sulphate and chloride. From pure calcium hydrogen carbonate solutions they favour the deposition of aragonite, although their influence is not very marked. The calcite deposited in the presence of aragonite nuclei never occurs in the form of sphæroliths and axioliths, although in the absence of these nuclei it is deposited preferably in these forms.

Nuclei of calcite have a very great effect and hinder, or very much limit, the deposition of unstable forms. From sea-water at 0°, the presence of calcite nuclei does not always prevent the deposition of Vater's modification (*Zeitsch. Kryst. Min.*, 1893, **21**, 433) and of the exceedingly unstable compound, $CaCO_3,6H_2O$.

The formation or greater stability of aragonite, Vater's modification, and hydrated calcium carbonate in sea-water is not due so much to the salt content as to the presence of magnesium salts. It is improbable that hydrated calcium carbonate plays any part in natural processes. Owing to the unfavourable solubility relations and to the slow establishment of equilibrium, the acceleration of the deposition of calcium carbonate from calcium hydrogen carbonate solutions is of very little importance so far as the formation of metastable modifications is concerned. T. S. P.

Carbides of Magnesium. I. J. Novák (*Zeitsch. physikal. Chem.*, 1910, **73**, 513—546. Compare Abstr., 1909, i, 865).—Magnesium was heated in a tube at a definite constant temperature, and a definite volume of a gaseous hydrocarbon passed over it. The products obtained in different experiments were decomposed by water, the acetylene converted into cuprous acetylide, the allylene into the silver compound (compare Berthelot, *Ann. Chim. Phys.*, 1866, [iv], **9**, 423), and from the relative amounts of these gases the composition of the residue was determined. It is shown that two carbides of magnesium, MgC_2 and Mg_2C_3, exist; they are decomposed by water according to the equations: $MgC_2 + 2H_2O = Mg(OH)_2 + C_2H_2$ and $Mg_2C_3 + 4H_2O = 2Mg(OH)_2 + C_3H_4$.

The decomposition of acetylene, accompanied by the formation of the carbide, MgC_2, begins about 400°; the proportion of the carbide

increases rapidly up to 490°, and beyond that point diminishes. Even at 700°, however, this carbide can still be detected in the reaction product. At 460° the presence of the carbide, Mg_2C_3, in the product can be proved; the proportion increases regularly up to 545°. At 714°, a large proportion of carbon is produced, and soon blocks up the tube. The products obtained between 465° and 515° are hard, compact masses, steel-grey in colour, and only decompose water slowly; those obtained above 550° are grey, brittle, and rapidly decompose water. The proportion of free carbon, formed by heating in a steel tube, is greater than when a porcelain tube is used, as in the above experiments.

With methane, the proportion of the carbide, Mg_2C_3, to free carbon produced is at first great, and only at 780° is the proportion of carbon the greater. The maximum point for the formation of Mg_2C_3 is 780°. The other carbide, MgC_2, could only be detected at 733°. The results with pentane and with octane are very similar to those with methane; the maximum in the formation of the carbide, Mg_2C_3, occurs in both cases about 700°. Of these three hydrocarbons, octane begins to decompose at the lowest temperature.

The results with benzene, toluene, and the three xylenes are somewhat similar to those for the three paraffins. In all cases the proportion of the carbide, MgC_2, is small, and the maximum formation of Mg_2C_3 occurs at temperatures ranging from 650° to 720°. The decomposition of toluene begins at the lowest temperature, 520°.

The relative proportions of the carbides and free carbon produced under different conditions are explained by the fact that at temperatures in the neighbourhood of 570°, the reaction $2MgC_2 \longrightarrow Mg_2C_3 + C$ is fairly rapid; this reaction predominates up to 610°, above which temperature the further reaction $Mg_2C_3 \longrightarrow Mg_2 + 3C$ becomes of most importance. The effect of temperature on the stability of the carbides is illustrated graphically. G. S.

[The Alloys of] Copper, Antimony, and Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 835—840).—Antimony and bismuth appear to form a continuous series of solid solutions, and an alloy containing 80% Bi, which, when first prepared, contains two structural constituents, becomes practically homogeneous after heating for ten days at 320°. Antimony does not retain copper in solid solution, the eutectic being distinctly present in an alloy containing 1·5% of copper. Copper does not retain more than a very minute quantity of antimony in solid solution. The ternary system is to be described. C. H. D.

New Compounds of Quadrivalent Cerium. GIUSEPPE A. BARBIERI and J. CALZOLARI (*Ber.*, 1910, **43**, 2214—2216).—Ceric salts may be obtained by oxidation of cerous salts with nitric acid when the acid of the cerous salt is non-volatile and does not react with nitric acid (compare Barbieri, Abstr., 1907, ii, 466). In this way *ceric selenite*, $Ce(SeO_3)_2$, *ceric dihydrogen arsenate*, $Ce(H_2AsO_4)_4,4H_2O$, and *ceric monohydrogen arsenate*, $Ce(HAsO_4)_2,6H_2O$, have been prepared.

Ceric selenite is prepared by heating 10 grams of cerous nitrate hexahydrate and 12 grams of selenious acid with 200 c.c. of nitric acid

(D 1·40) under reflux for some hours. It is an orange-yellow powder, insoluble in water, but slightly soluble in concentrated nitric acid

Ceric dihydrogen arsenate is formed by heating cerous nitrate (1 mol.) and arsenic acid (4 mols.) with concentrated nitric acid for some hours. After distilling off the excess of nitric acid, the pale yellow solution deposits white needles of the above salt. When it is dissolved in the minimum quantity of concentrated nitric acid and the cold solution diluted with water, a white, crystalline deposit of *ceric monohydrogen arsenate* is formed, arsenic acid remaining in solution. T. S. P.

Thermic Reduction of Alumina. PAUL ASKENASY and A. LEBEDEFF (*Zeitsch. Elektrochem.*, 1910, **16**, 559—566).—As previous observers have obtained contradictory results on the reduction of alumina by carbon, a complete review of the literature is given. The authors have made experiments with direct and alternating current arc furnaces and with an electrical resistance furnace. A mixture of alumina and wood charcoal heated in an arc furnace (similar to those employed in making calcium carbide) gives off large quantities of carbon monoxide at first followed by brilliant flames of burning aluminium vapour. If the heating is stopped as soon as these appear, the product consists of fused alumina mixed with aluminium carbide and aluminium. In the carbon tube resistance furnace, the highest temperature reached was not much above the melting point of alumina (about 2000°), and here, too, both carbide and metal were formed. Aluminium carbide is not changed when heated in a vacuum at any temperature between 400° and 1400°. The authors think that aluminium carbide is first formed : $2Al_2O_3 + 9C = Al_4C_3 + 6CO$. This reacts with alumina (or dissociates) at higher temperatures (2100°, say), yielding aluminium, which may probably be dissolved in the carbide (otherwise it would distil away because its boiling point is about 1800°); on cooling, the aluminium separates out of the solution, which explains why aluminium and its carbide were found side by side in the product. T. E.

Advances in the Domain of the Ceramic Industry. WILHELM PUKALL (*Ber.*, 1910, **43**, 2078—2106).—An account of the history of, and recent advance in, the domain of the ceramic industry. J. J. S.

Manufacture of Cementation Steel. VII. Cementation based on the Specific Action of Carbon Monoxide. FEDERICO GIOLITTI and G. TAVANTI (*Atti R. Accad. Sci. Torino*, 1910, **45**, 539—563).—It is shown that fracture frequently takes place in steels along a boundary between two portions of different structure, due to segregation, the proportion of carbon being different on the opposite sides of the line of fracture. This segregation occurs during the slow cooling of the steel, and it is, therefore, desirable to find a process of cementation (case hardening) in which such segregation is avoided.

The steel is heated in a porcelain tube, the ends of which are packed with purified carbon, whilst a current of carbon dioxide is led slowly through the tube. The steel is then in contact with a mixture of carbon monoxide and dioxide in equilibrium with carbon at the given

temperature. The steel preserves its bright surface during the process of cementation. The carbon is in this way much more evenly distributed in the outer layers of the steel than when ethylene is used, and the brusque transition from high to low carbon steel in the outer zone does not occur. C. H. D.

Thorium Sulphate. BARRE (*Compt. rend.*, 1910, **151**, 231—234). —Experiments have shown that aqueous solutions of thorium sulphate have a specific resistance and freezing point in good agreement with the laws of Bouty and Raoul. Similar cryoscopic and conductivity determinations have confirmed the existence of the double sulphate of potassium and thorium described in a previous communication (this vol., ii, 718). W. O. W.

Mineralogical Chemistry.

Analyses of Seligmannite, Zinciferous Tennantite, and Fuchsite from Binn, Switzerland. GEORGE T. PRIOR (*Min. Mag.*, 1910, **15**, 385—387).—The following analyses are given of minerals from the crystalline dolomite in the Lengenbach quarry. The rare mineral seligmannite, described by H. Baumhauer in 1901, has not previously been analysed; but from a consideration of the crystalline form it was predicted to be the sulpharsenite of copper and lead, $CuPbAsS_3$, isomorphous with bournonite ($CuPbSbS_3$). This prediction is fully confirmed by the following analyses: I agrees closely with the above formula, while the material of II was perhaps not quite so pure:

	Pb.	Cu.	Ag.	Zn.	Fe.	As.	Sb.	S.	Total.	Sp. gr.
I.	46·34	13·09	0·11	0·27	0·06	16·88	0·64	21·73	99·12	5·44
II.	48·83	10·51	0·23	—	0·80	16·94	0·71	22·01	100·03	5·48
III.	—	42·03	1·24	7·76	0·62	19·80	—	28·08	99·53	4·61

Analysis III is of zinciferous tennantite ("binnite") with the form of cubes, the faces of which are deeply striated parallel to one diagonal, this is, parallel to the edges of intersection with small tetrahedral faces.

Clear, green crystals of muscovite (fuchsite) gave:

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	Loss on ignition.	Total.
47·24	31·86	0 87	0·56	0·58	2·91	10·72	0·16	0·14	5·37	100·41

L. J. S.

Minerals Formed by the Combustion of Pyritous Shales in Midlothian. S. JAMES SHAND (*Min. Mag.*, 1910, **15**, 403—406).—By the spontaneous combustion of a heap of shaly refuse at the Emily coal pit, Arniston, the following minerals have been formed: Native sulphur, as powdery encrustations and as minute crystals. Sal-

ammoniac, as fibrous crusts and small rhombic-dodecahedra. Tschermigite (?) (ammonia-alum) was detected amongst the material by qualitative tests. Mascagnite (ammonium sulphate), as fibrous and mealy encrustations. Halotrichite (?), as white to yellow, porous masses cementing fragments of cinder and burnt shale. When taken from the hot refuse heap this had a fused appearance, but it soon deliquesced on exposure to air. It is suggested that the white portion of this material may, while still hot, have been anhydrous aluminium sulphate (which would represent a new mineral species). Analysis of the portion soluble in water gave:

Al_2O_3.	Fe_2O_3.	CaO.	SO_3.
20·44	10·57	1·08	67·91

corresponding with

$Al_2(SO_4)_3$.	$Fe_2(SO_4)_3$.	$CaSO_4$.	H_2SO_4.
68·13	26·28	2·62	2·97

L. J. S.

Rivotite. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1910, **33**, 190—192).—This name was applied by Ducloux, in 1874, to a compact, yellowish-green material from Spain; his analysis showed: Sb_2O_5, 42·00; Ag_2O, 1·18; CuO, 39·50; CO_2, 21·00 = 103·68. A very similar material is now being worked as an ore at Irazein, near Sentein, dep. Ariège, France, where it forms bead-like masses in dolomites of Devonian age. This is olive-green or blackish-green with a dull, uneven fracture, and it sometimes encloses specks of tetrahedrite and strings of malachite and chessylite. To all appearance the material is homogeneous, but thin sections under the microscope show around grains of tetrahedrite concentric layers of a golden-yellow isotropic material and of a greenish-yellow birefringent material. The latter is dissolved out by ammonia or by acetic acid, and consists of malachite, whilst the former is a hydrated oxide of antimony soluble in hydrochloric acid. The original Spanish material presents the same microscopical characters, and was proved to contain water. Rivotite is therefore an intimate mixture of malachite and stibiconite resulting from the alteration of tetrahedrite.

L. J. S.

Datolite from the Lizard District, Cornwall. W. F. P. MCLINTOCK (*Min. Mag.*, 1910, **15**, 407—414).—A new occurrence of crystallised datolite (a mineral only once before recorded in England) has been discovered at the junction of a serpentine and hornblende-schist at Park Bean Cove in the parish of Mullion. The associated minerals in the crystal-lined cavities are calcite, rarely natrolite, and specks of copper-pyrites. Massive datolite and the botryolite variety are also present. A detailed crystallographic description is given, and the optical constants determined. The following analysis agrees closely with the usual formula: $HCaBSiO_5$.

SiO_2.	CaO.	$(Fe,Al)_2O_3$.	B_2O_3.	H_2O.	Total.	Sp. gr.
37·45	34·67	0·57	21·87	5·67	100·23	3·001

L. J. S.

A Soda-sanidine from Mitrowitza. Franz Angel (*Jahrb. Min. Beil. Bd.*, 1910, **30**, 254—268).—The analysis of a soda-sanidine from Mitrowitza gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.
62·04	21·60	2·29	0·95	0·53	6·73	4 92	99·06

corresponding with $8KAlSi_3O_8$, $9NaAlSi_3O_8$.

Crystallographic investigations show that it is really an orthoclastic felspar with unusually abnormal optical orientation. It stands in the same relation to the soda orthoclases as does the normal sanidine to ordinary orthoclase. T. S. P.

A New Mineral from the Iron Mines near Segré (Maine-et-Loire). Alfred Lacroix (*Bull. Soc. franç. Min.*, 1910, **33**, 270—273).—This mineral, which has previously been considered as biotite, occurs in a vein, together with chalybite, quartz, and some galena, at the junction of beds of magnetite with an altered diorite in the Minguet mine. It forms confused aggregates of opaque, black or greenish-black plates, somewhat resembling stilpnomelane in appearance. In convergent polarised light a dislocated black cross is seen, the optical sign being negative. The very strong dichroism is black and opaque to clear yellow. Before the blowpipe the mineral fuses to a black magnetic enamel; and all the water is lost at a low red-heat. It is easily attacked by hydrochloric acid, leaving pearly scales of silica. Analysis by F. Pisani gave the following results, agreeing with the formula: $17SiO_2,4(Fe,Al)_2O_3,8(Fe,Mg)O,K_2O,8H_2O$.

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
43·65	5·22	18·80	19·00	3·22	0·94	0·66	3·00	6·00	100·49	2 86

The mineral thus differs from the micas in the small amount of alumina and alkalis, and also in the water being expelled at a lower temperature. It approaches more nearly to stilpnomelane, from which, however, it differs in containing alkalis and much ferric iron. Since the chlorites are characterised by the absence of alkalis, the name *minguetite* is proposed for this mineral, which in composition is intermediate between the iron-mica lepidomelane and the iron-chlorite stilpnomelane. L. J. S.

Structure and Composition of the Chandakapur Meteoric Stone. Herbert L. Bowman and Herbert Edmund Clarke (*Min. Mag.*, 1910, **15**, 350—376).—A description is given of one of three meteoric stones which fell near Chandakapur, in the Berar valley, India, on June 6, 1838. The structure is chondritic. Full details are given of the methods of analysis; briefly these are: (i) A preliminary separation of the magnetic material from the dry powder by means of a magnet, and the extraction of the metallic constituents from the two portions so obtained, by the prolonged action of a solution containing mercuric chloride, in an atmosphere freed from oxygen. (ii) The reduction of rust, magnetite, sulphides, and phosphides to the metallic state by ignition in hydrogen, and extraction of the resulting metals with mercuric solution. (iii) The separation of the silicates into two

portions, by treatment with hydrochloric acid under conditions favourable to the attack of olivine but not of pyroxene or felspar. (iv) The analysis of the resulting fractions and the estimation of alkalis and of sulphur and phosphorus by the usual analytical methods.

The combined results give the following bulk composition of the meteorite:

Metallic.			Combined as schreibersite and troilite.					
Fe.	Ni(Co).	Cu.	Fe.	Ni(Co).	P.	S.	Rust and magnetite.	Chromite.
5·25	0·55	trace	3·73	0·31	0·16	1·79	0·3	0·51

SiO_2.	MgO.	FeO.	CaO.	NiO.	Al_2O_3.	Na_2O.	K_2O.	Total.
38·02	21·31	19·81	2 42	0·07	4·17	1·26	0 29	99·95

The corresponding mineralogical composition is:

Metallic alloys.	Troilite.	Schreibersite.	Chromite.	Rust and magnetite.	Olivine (and some "glass").	Pyroxene (and felspars).
5·80	4·92	1·06	0·51	0·30	53·47	33·89

L. J. S.

Physiological Chemistry.

What Influence does the Exact Estimation of the Tension of Water Vapour Exert on the Results Obtained in the Respiration Experiments in the Regnault-Reiset Apparatus as Modified by Zuntz and Oppenheimer. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1910, **27**, 147—169).—In calculating the volume of oxygen and nitrogen in the apparatus at the beginning and end of the experiment, it has been generally assumed that the air is saturated with water-vapour. This the author shows is not the case, and he calculates the possible errors due to the neglect of this fact. He corrects for the error by estimating the degree of saturation of air in the apparatus by means of a hygrometer, and gives experimental examples to show how by this means the error can be reduced, illustrating his points both by combustion of alcohol in the apparatus and by actual respiration experiments on infants. S. B. S.

Periodic Breathing at High Altitudes. The Estimation of Total Oxygen Capacity and Blood-volume at Different Altitudes by the Carbon Monoxide Method. C. GORDON DOUGLAS (*J. Physiol.*, 1910, **40**, 454—471, 472—479).—Increase of altitude increases the duration of the periodic breathing which follows apnœa produced by forced breathing; indeed, Cheyne-Stokes breathing may at a sufficient altitude become permanent. The cause is deficiency

of oxygen. Circulatory changes may intensify the condition, but psychic influence is negligible.

Determinations of the total oxygen capacity in the same individual by the carbon monoxide method give variations ± 8% of the mean value. At high altitudes partial saturation of the observer with carbon monoxide renders him, comparatively speaking, inefficient to make colorimetric observations. Fallacy may also arise from the experiment lasting too short a time for thorough admixture of the whole blood and the gas to occur. W. D. H.

The Influence of Oxygen Pressure on the Gaseous Exchange of Certain Sea Animals. MARTIN HENZE (*Biochem. Zeitsch.*, 1910, **26**, 255—278).—The animals were kept in closed vessels at constant temperature in sea-water with varying contents. The oxygen was estimated in the water by Winkler's method before and after the experiments. There was generally found to be a certain maximum oxygen concentration, beyond which the oxygen consumption did not increase. The oxygen consumption in the case of fertilised eggs was independent of the oxygen content of the water. S. B. S.

Respiratory Quotients after Exclusion of the Abdominal Organs. OTTO PORGES (*Biochem. Zeitsch.*, 1910, **27**, 131—142).—It was found that in rabbits with artificial respiration, in which the abdominal organs had, by means of ligatures, been excluded from the circulation, the respiratory quotient was higher than in control animals treated in the same way, but in which circulation through the abdominal organs remained intact. The author interprets the result as indicating that only carbohydrates are utilised under the former conditions, as the fats and proteins can only be utilised when the liver is intact; these substances probably undergo such changes in that organ that carbohydrates can be formed from them. S. B. S.

The Respiratory Quotients of Dogs with Pancreatic Diabetes when the Abdominal Organs are Excluded from the System. OTTO PORGES and H. SALOMON (*Biochem. Zeitsch.*, 1910, **27**, 143—146).—As the respiratory quotient is higher in diabetic animals with abdominal organs excluded from the circulation than in similar control animals with circulation intact, the conclusion is drawn that in diabetes the capacity of the organism for burning sugar remains intact. S. B. S.

The Distribution of Reducing Substances in Rabbit's Blood. H. LYTTKENS and J. SANDGREN (*Biochem. Zeitsch.*, 1910, **26**, 382—390).—The reducing substances were estimated by Bang's method in serum, corpuscles, etc., both before and after submitting the protein-free liquids to fermentation. It was found that both serum and corpuscles contain reducing substances. In the corpuscles the quantity is from 0·07 to 0·08, and in the serum 0·27% (calculated as dextrose). Sucrose appears to be absent. After bleeding, the reducing substances increase to 0·14% in the case of the corpuscles, and to 0·60% in the case of serum. After phloridzin poisoning, the content

in reducing substances is the same as in normal blood; and after adrenaline, about the same as in animals after blood-letting. A part of the sugar in circulating blood exists apparently in a form of combination. The whole of the sugar is in the serum (normal quantity, 0·22%). The remainder of the reducing substance is not sugar (conclusions from fermentation tests). S. B. S.

Conjugation as Sulphonyl Derivatives. EDUARDO FILIPPI (*Chem. Zentr.*, 1910, i, 1981; from *Arch. Farm. sperim.*, 1910, **9**, 158—172).—Small quantities of phenol in blood can be detected by physical changes, such as conductivity, freezing-point depressions, surface-tension, etc. After injection of phenol, guaiacol, and thiocol (potassium guaiacolsulphonate), free phenols can be detected in the blood by these physical or chemical methods only for a short time, and in small quantities, even after addition of toxic doses. Even after one to two hours, the phenols circulate in the form of sulphuric acid esters. S. B. S.

Relation of the Pancreas to Blood Diastases in Dogs. H. OTTEN and T. C. GALLOWAY, jun. (*Amer. J. Physiol.*, 1910, **26**, 347—353).—After extirpation of the pancreas, the diastases of the blood are either destroyed or eliminated in a short time. Later, they again appear, showing that the pancreas is not the sole seat of their origin, although it is probably an important one. The point is discussed whether the blood diastases are related to sugar metabolism or are waste products, or whether they are of two kinds: (1) those of pancreatic origin of no significance in metabolism, and (2) those from other organs (possibly the liver), which may play an important part in the destruction of glycogen. W. D. H.

The Nature of the Antitrypsin Formation in the Organism. A. BRAUNSTEIN and L. KEPINOFF (*Biochem. Zeitsch.*, 1910, **27**, 170—173). —The authors contend that the increased formation of antitrypsin in blood-serum is due to cell degradation, and the setting free of the intracellular, proteolytic, or autolytic ferments. They show that the antitryptic action of the serum can be increased by the injection intraperitoneally of liver or carcinoma paste if the material is not previously heated. If it is heated before injection, no increased antitrypsin formation is observed. S. B. S.

Quantity of Secretion in a Given Gastric Fluid. JUSTIN WINTER (*Compt. rend.*, 1910, **151**, 165—167).—A discussion of the influence of test meals on the concentration of the gastric fluid.
W. O. W.

Calcium Metabolism and its Relationship to Phosphoric Acid and Magnesium Metabolism. MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1910, **27**, 85—86).—In an adult dog, it is impossible under normal conditions to determine a minimum of calcium necessary for maintenance of equilibrium, since the calcium balance is influenced by the amounts of ingested protein, fat, and probably also carbohydrate,

for by adding these to the original diet, a considerable quantity of calcium is eliminated by the organism. Calcium equilibrium can be reconstituted by the addition of calcium to the increased diet. For these reasons, the calcium equilibrium can be varied at will. Magnesium behaves in a similar way. Phosphoric acid metabolism is influenced by the amount of protein and calcium ingested. The peculiar behaviour of the lime is explained by assuming that the excess is rendered harmless by entering into combination with the harmful or unused metabolites, and thus eliminated from the body. S. B. S.

The Influence of Long-continued Ingestion of Nucleic Acid on the Purine Metabolism and the Excretion of Allantoin in the Dog. WAICHI HIROKAWA (*Biochem. Zeitsch.*, 1910, **26**, 441—457).—A small dog could tolerate for three months 5 grams of sodium nucleate daily added to a mixed, but fairly uniform, diet without suffering any ill effects. The purine bases ingested in this form were excreted chiefly as allantoin, and only a small portion in the form of uric acid or purine bases, even on superimposition of lead poisoning. About 72—88% of the ingested purine bases appeared in the urine in the form of purine substances or allantoin. Every gram of the ingested bases corresponded with an increased output of 0·0519 gram of nitrogen in the urine in the form of purine substances or allantoin. With long-continued feeding, the amount of allantoin excreted decreased, whereas that of uric acid increased, until after ten weeks the amount of uric acid was about ten-fold that of the first week. Lead poisoning caused a still greater increase. At the beginning of the nucleic acid ingestion, the uric acid nitrogen was about 1% of the sum of the purine and allantoin nitrogen; it afterwards increased to 13% without any corresponding increase of the purine base nitrogen. During the ingestion of excess of purine bases, therefore, the organism loses its capacity of oxidising uric acid to allantoin. S. B. S.

The Physiology of Winter Sleep. FELIX REACH (*Biochem. Zeitsch.*, 1910, **26**, 391—405).—Dormice lose during the first two months of their winter sleep on an average 0·26% of their body-weight daily, of which more than half is attributable to loss of fat. No glycogen was formed during winter sleep, in fact, a certain quantity was lost. Whilst the absolute quantity of this substance lost was small compared with the fat, the relative proportions of these two substances as compared with their total quantity stored in the animal body was about the same. During the sleep both the fat and glycogen accumulated in the liver. The quantitative composition of the fat did not alter very much during the winter sleep; those acids, however, with the molecule smaller than that of palmitic acid appeared to be destroyed first; the other fatty acids gave no evidence of change, nor could an increase of the hydroxy-acids be ascertained. S. B. S.

Changes in the Fats of the Hen's Egg during Development. ELIZABETH C. EAVES (*J. Physiol.*, 1910, **40**, 451—453).—As the fat decreases in the yolk, that in the chicken increases; there is some loss

due to fat being used to furnish energy; the low respiratory quotient indicates utilisation of fat. During the first ten days of incubation the iodine value of the yolk fat falls from 70 to 64, and after this to 44; that of the chicken fat is at first low and rises later. The low value at first may be due to the presence of other substances (especially a brown substance, supposed to be glycerol and glycero-phosphoric acid) in the fat. The increase later points to a desaturation of the absorbed fat. The theory of Leathes, that the formation of double linkings is the first step in the oxidation of fat, is supported. W. D. H.

Inhibition of the Toxic Action of Hydroxyl Ions on the Eggs of the Sea-Urchin by means of Potassium Cyanide. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, **26**, 279—288).—The author assumes that hydroxyl ions act toxically by accelerating oxidation. By withdrawal of oxygen, or the addition of potassium cyanide, this oxidative process can be inhibited. If either fertilised or unfertilised eggs of *Strongylocentrotus purpuratus* were placed in artificial sea-water (50 c.c. of 0·54% *m*-NaCl + 1·1 c.c. *m*/2-KCl) containing excess of alkali, and then transferred to normal sea-water and fertilised, they did not develop normally. In a control experiment in which potassium cyanide in addition to alkali was added, normal development proceeded. The author discusses the theory of the action of alkali on fertilised and unfertilised eggs. S. B. S.

Inhibition of the Toxic Action of Hydroxyl Ions on the Unfertilised Egg of the Sea-Urchin by Withdrawal of Oxygen. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, **26**, 289—292). —One set of eggs was kept in sodium chloride solution and alkali in the presence of a current of air, and the other was kept under similar conditions, but in presence of hydrogen. Those eggs kept under the former conditions were rapidly destroyed, whilst the others could be kept for some hours, and, after transference to sea-water and fertilisation, developed in the normal way. If kept for too long under these conditions, however, they could not be developed. (For theory, see preceding abstract.) S. B. S.

The Distribution in the Organs of Ferments Capable of Splitting Asparagine. OTTO VON FÜRTH and M. FRIEDMANN (*Biochem. Zeitsch.*, 1910, **26**, 435—440).—A ferment capable of liberating ammonia from asparagine was found in all organs. The method of experiment was to determine the amount of ammonia set free by similar portions of organs incubated with and without asparagine. In the case of the mucous membrane of the small intestine, the amount of ammonia liberated was so great as to indicate the scission of this substance from the amino- as well as from the amido-group. S. B. S.

Hæmolysis in the Liver. LEONARD FINDLAY (*J. Physiol.*, 1910, **40**, 445—450).—The blood of the hepatic vein contains in the majority of experiments recorded more red corpuscles than that of the portal vein; this is probably due to lymph formation and consequent

concentration of the blood. The hæmoglobin roughly runs a parallel course. No free hæmoglobin occurs in hepatic blood. The experiments, therefore, lend no support to the view that hæmolysis occurs in the liver. The animals experimented with were cats.

W. D. H.

The Inhibition of Acetoacetic Acid Formation in the Liver. GUSTAV EMBDEN and JOSEPH WIRTH (*Biochem. Zeitsch.*, 1910, 27, 1—19).—The authors, by perfusion experiments, have already shown that certain substances give rise to acetone substances in the liver (leucine, *iso*leucine, tyrosine, phenylalanine, etc.). They now show that other substances, when added to these in the blood-mixture used for perfusion, inhibit the increased formation of acetone substances. Amongst such substances are *n*-valeric acid, amino-*n*-hexoic acid, and, to a less degree, *iso*hexoic acid. The inhibitory character depends apparently on the combustibility of these substances in the liver; when these are present, the substances giving rise to acetone substances are acted on so slowly, the acetoacetic acid, etc., formed so slowly, that they are destroyed without accumulating. A high content of glycogen in the liver also inhibits the acetone formation from *iso*valeric acid, although dextrose is without effect on this factor. From this fact, the conclusion is drawn that stored glycogen is more readily burnt than dextrose. *dl*-Alanine and *dl*-lactic acid are also without effect on acetoacetic acid formation; no definite conclusions could be drawn as to the action of glycerol.

S. B. S.

Acetoacetic Acid Formation in the Liver of a Diabetic Dog. II. WALTER GRIESBACH (*Biochem. Zeitsch.*, 1910, 27, 34—37). —It has been shown by Embden and Wirth (preceding abstract) that the addition of *n*-valeric acid inhibits the formation of acetone when substances which are normally acetone formers are perfused through the liver. In dogs which have been rendered glycosuric either by pancreas extirpation or phloridzin, this inhibition by *n*-valeric acid does not take place. The explanation of this fact which is considered most probable by the author is, that the livers of animals which have been rendered diabetic have so much fat stored up intracellularly, which is so readily combustible with formation of acetone substances, that the addition of other added combustible substances, such as *n*-valeric acid, exerts no influence on the formation of acetone substances.

S. B S.

The Degradation of *iso*Leucine in the Liver. JOSEPH WIRTH (*Biochem. Zeitsch.*, 1910, 27, 20—26).—When *iso*leucine or α-methylbutyric acid, which is assumed to be an intermediary degradation product of the former, are perfused through the liver there is sometimes an increased formation of acetone substances, and at other times not. There are various ways by which degradation can take place, as either the methyl or the ethyl group can be oxidised. In the former case only is an acetone-forming substance formed. That the ethyl group can also be destroyed is shown by the experiments with β-methylvaleric acid, which on perfusion gives rise to increased formation of

acetone substances, the formation of which can only arise by the destruction of the ethyl group. Ethylbutyric acid also gives rise to variable results. S. B. S.

Degradation of Leucine in the Liver. FRITZ SACHS (*Biochem. Zeitsch.*, 1910, **27**, 27—33).—It has been shown that amino-acids behave in the liver with regard to the formation of acetone substances like the amino-free acid containing one carbon atom less, and not like those with the same number of carbon atoms. From this it appears as if the amino-acids are degraded by deamidisation and oxidation of the terminal carbon atom. If oxidation takes place before deamidisation, the possible intermediate product in the degradation of leucine is *iso*amylamine, from which by deamidisation, *iso*amyl alcohol, *iso*valeraldehyde, and *iso*valeric acid can be produced. If deamidisation precedes oxidation, the immediate products would be *iso*butylhydroxyacetic (leucic) acid, from which by deamidisation and scission of carboxyl group, *iso*amyl alcohol, etc., would be produced. To gain an insight into the method of degradation of leucine, the behaviour of these various substances with regard to acetone formation in the liver was investigated. All the above substances were found to be powerful acetone-formers, with the exception of *iso*amyl alcohol, which in larger doses was toxic to the liver. No definite conclusions could be drawn from these experiments, therefore, as to the method of leucine degradation No marked difference was found between the behaviour of *l*-leucic acid and *dl*-leucic acid, which is in marked contrast to what has been found in the case of *l*-leucine and *dl*-leucine. S. B. S.

Liver Functions (Deamidation, Reduction, and Carbon Dioxide Cleavage in the Artificially Perfused Liver). OTTO NEUBAUER and HANS FISCHER (*Zeitsch. physiol. Chem.*, 1910, **67**, 230—240).—If the surviving liver of the dog is perfused with a mixture of dog's blood and Ringer's solution, and phenylaminoacetic acid added, the *d*-component is so altered that the *l*-acid remains in excess. The deamidised product of the amino-acid is the corresponding ketonic acid (phenylglyoxylic acid). Secondarily, this is reduced to *l*-mandelic acid, and, in part, changed into benzoic acid. Whether other tissues behave in a similar way has yet to be tested, but the evidence available is in favour of the liver being the principal seat of such changes. W. D. H.

Tyrosine Catabolism in the Artificially Perfused Liver. OTTO NEUBAUER and WALTER GROSS (*Zeitsch. physiol. Chem.*, 1910, **67**, 219—229).—The method adopted for perfusion is described with full detail; by practice the perfusion with dog's blood diluted with Ringer's solution can be commenced ten minutes after the excision of the liver; the amount of acetone in the outflowing fluid is increased, as Embden showed; the addition of *p*-hydroxyphenylpyruvic acid leads to an enormous increase of acetone similar to that produced by the addition of a corresponding quantity of tyrosine. The addition of *p*-hydroxyphenyl-α-lactic acid has no such effect. These results, together with those obtained in metabolic experiments on alcaptonuric patients,

support the hypothesis that the ketonic acid, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, is the normal product of intermediate tyrosine metabolism, and not the alcohol acid, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$. W. D. H.

The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour During Autolysis. I. Does the Liver Contain Cholesterol Esters? KENRO KONDO (*Biochem. Zeitsch.*, 1910, **26**, 238—242).—An alcoholic extract of livers was made, from which the alcohol was evaporated off. An extract with ethyl acetate was made of the residue, and the "acetyl number" of the substances extracted was determined both before and after hydrolysis with alcoholic potassium hydroxide. From the fact that this number is larger after hydrolysis than before, the conclusion was drawn that cholesterol esters were present, and that, in fact, about 39% of the total cholesterol in the organ existed in the form of esters. The same results were obtained if the experiment was carried out after precipitation of the free fatty acids in the ethyl acetate extract by methyl-alcoholic barium hydroxide before determination of the acetyl numbers. The results are not due, therefore, to water-insoluble fatty acids. These results are not in accordance with those previously obtained by Nakada, working with a somewhat different method. S. B. S.

The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour during Autolysis. II. Does the Liver contain an Enzyme Capable of Splitting Cholesterol Esters? KENRO KONDO (*Biochem. Zeitsch.*, 1910, **26**, 243—251).—An emulsion of oleic acid, olive oil, and cholesteryl oleate showed, on incubation with unboiled (but not with boiled) liver extracts, a greater increase in the acetyl number than was shown if the extract alone was incubated. An increase in the acetyl number also took place when an oleic acid emulsion alone was treated with liver extracts. The results do not show conclusively whether an enzyme capable of splitting cholesterol esters was present, as they can be taken to indicate that oxidation of oleic acid to form substances with a larger number of hydroxyl groups can also have taken place. S. B. S.

The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour during Autolysis. III. The Formation of Hydroxy-Fatty Acids during Autolysis of the Liver. KENRO KONDO (*Biochem. Zeitsch.*, 1910, **26**, 252—254).—The acids obtained by precipitation of the ethyl acetate extracts (see preceding abstracts) by methyl-alcoholic barium hydroxide were added to the fatty acids obtained by hydrolysis from that part of the alcoholic extract of the liver which was not soluble in ethyl acetate. The acetyl number of the acids thus obtained was determined in equivalent portions of the liver extract both before and after autolysis. The increase in the acetyl number after autolysis indicated the formation of fatty acids during this process. S. B. S.

The Importance of the Skin as a Depôt of Chlorine. J. H. PADTBERG (*Arch. exp. Path. Pharm.*, 1910, **63**, 60—79).—On food either rich or poor in chlorides, the skin, blood, kidneys, and lungs contain

the highest, and the muscles the lowest, percentage of chlorine. On food rich in chlorides, the chlorine in the dog rises on the average 0·17%; on food poor in chlorides, it falls 0·137%; by intravenous injection of hypertonic salt solution, it rises 0·2%. On chlorine-poor food, the skin contains about one-quarter of the total chlorine in the body; on chlorine-rich food, this rises to one-third. After intravenous injection, the rise in chlorides is greatest in the skin; the lungs, intestine, blood, and kidneys follow in the order named. W. D. H.

Phosphorus in Beef. II. C. K. FRANCIS and PERRY F. TROWBRIDGE (*J. Biol. Chem.*, 1910, **8**, 81—94. Compare this vol., ii, 731).—A large number of analyses of the different organs and cuts in various steers and cows are given. In young animals the results are fairly uniform, but this is not so in mature animals. The largest amount of phosphorus is found in the circulatory and nervous systems. In thin animals the results are usually lower. Further generalisation does not appear at present possible. W. D. H

The Glycogen Content in Tunicates; the Influence of Iron on the Estimation of Glycogen. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, **27**, 53—60).—In tunicates (ascidea), in addition to cellulose, another polysaccharide (glycogen) is present in considerable quantities (not less than 26% of the dry weight of the organs). A diastatic ferment is also present, which is capable of acting at relatively low temperatures. In the course of the investigations it was found that an error existed in Pflüger's method for the estimation of glycogen, due to the presence of iron, which, in the form of hydroxide, is capable of absorbing considerable quantities of the polysaccharide. For this reason, after the tissues have been treated with alkali, the insoluble portion should also be examined, as it contains glycogen absorbed by the iron. This portion should be dissolved in hydrochloric acid, and the glycogen in the solution thus obtained determined. By neglecting this operation, an error of as much as 50% can be made in the glycogen determinations in certain cases. S. B. S.

The Secretion of Cholesterol in Human Bile. BACMEISTER (*Biochem. Zeitsch.*, 1910, **26**, 223—230).—The amount of cholesterol secreted in four cases of human biliary fistula was investigated, the alcohol being estimated by the digitonin method of Windaus. The output altered greatly from day to day; the average in the four cases varied between 0·11 and 0·23 gram daily. It was, however, appreciably lower immediately after the operation. S. B. S.

The Alleged Occurrence of Trimethylamine in Urine. C. C. ERDMANN (*J. Biol. Chem.*, 1910, **8**, 57—60).—The volatile character of trimethylamine suggested that Folin's air current method which he uses for ammonia estimations might be employed. The test employed was the characteristic odour which Kaufmann states can be detected in dilutions as low as 1 in two millions. No trimethylamine could be detected in ten normal urines. It can be obtained from stale urine, or from any urine which has been subjected to Kjeldahl digestion.

W. D. H.

The Presence and Detection of Allantoin in Human Urine. KARL ASCHER (*Biochem., Zeitsch.*, 1910, **26**, 370—381).—The allantoin was obtained in crystalline form after precipitation by Wiechowski's reagent (mercuric acetate in sodium acetate solution), which was added after freeing the urine from various constituents by phosphotungstic acid and silver nitrate, and other treatment. In the case of a normal individual, 8 mg. of allantoin were recovered for one day's output of urine; in the case of a starving man, 1 mg. was obtained, and in a case of leucæmia, 5·6 mg. Allantoin was absent in a case of pernicious anæmia, and its presence was doubtful in a case of Addison's disease. Allantoin is readily adsorbed by animal charcoal under certain conditions to the extent of more than 90%. The author finds that the naphtharesorcin test is not applicable, as under certain conditions colours can be obtained from the reagent itself in blank tests; neither is the peptone-sulphuric acid reagent applicable to urine.

S. B. S.

The Occurrence of Creatine in Diabetic Urine. R. A. KRAUSE and WILHELM CRAMER (*Proc. physiol. Soc.*, 1910, lxi—lxii; *J. Physiol.*, **40**).—In typical diabetes mellitus, and in phloridzin glycosuria (in dogs), creatine is regularly found in the urine. It was also found in eight cases of pregnancy at the seventh or eighth month. Creatine occurs in all conditions that may lead to acidosis or to muscular atrophy. Creatine may appear before acidosis sets in, as in the cases of diabetes examined. W. D. H.

Formation of Sugar from Fat (in Phloridzin Diabetes). FELIX LOMMEL (*Arch. exp. Path. Pharm.*, 1910, **63**, 1—9).—It was thought that some light might be thrown on this vexed question by the administration of alcohol to dogs rendered diabetic with phloridzin. If sugar originates from fat, the removal of fat by alcohol would lessen the glycosuria, or cause some change in the dextrose : nitrogen ratio. The experiments gave varying and therefore disappointing results.

W. D. H.

Alleged Anæsthetic Properties of Magnesium Salts. CHARLES C. GUTHRIE and A. H. RYAN (*Amer. J. Physiol.*, 1910, **26**, 329—346).—The authors do not agree with Meltzer and Auer that magnesium sulphate is very toxic, and that it has specific anæsthetic effect. The immobility after large doses is due rather to the effect on the neuro-muscular apparatus; if this produces, as it generally does, more or less asphyxia, loss of sensation is due to the asphyxia, and its amount will depend on the degree of asphyxiation. W. D. H.

Narcotics and Local Anæsthetics. II. OSCAR GROS (*Arch. exp. Path. Pharm.*, 1910, **63**, 80—106. Compare this vol., ii, 529).—The theory of narcosis of Hans Meyer and Newton applies to local anæsthetics; the bases of local anæsthetics act more strongly than their salts. The anæsthetic potential of the salt depends on that of the base, and the degree of hydrolytic dissociation; that of novocaine

hydrogen carbonate is five times greater than that of the chloride. The bases of all the local anæsthetics investigated are about equal in strength, and affect sensory more readily than motor nerves. Eucaine and stovaine have the strongest, and novocaine the weakest, affinity for protein.
W. D. H.

Action of Praseodymium, Didymium, and Erbium on the Frog's Heart. GEORGE R. MINES (*Proc. physiol. Soc.*, 1910, lxviii; *J. Physiol.*, 40).—The chlorides of the elements mentioned act in the same way as other rare earths. Neutral Ringer's solution containing 0·00001 mol. per litre stops the ventricle in a few minutes. Washing out with neutral Ringer's solution causes slow and imperfect recovery. The addition of a little alkali renders it prompt and complete. The fact that didymium and praseodymium tested alternately on the same heart show the same activity renders it probable that neodymium, the other constituent of didymium, has the same action as praseodymium.
W. D. H.

The Degradation of Carboxylic Acids in the Animal Body. IX. The Behaviour of *p*-Chlorophenylalanine, *p*-Chlorophenylpyruvic Acid, and *p*-Chlorophenyl-lactic Acid in the Animal Body. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, 27, 97—112. Compare Abstr., 1908, ii, 719).—In the conversion of tyrosine into homogentisic acid in the organism, it has been assumed that a quinol derivative is formed as an intermediate product; this can only happen when an α-hydroxyl group exists, or can be introduced into the para-position of the other substituting group. For this reason it was of interest to investigate the behaviour of those substances in which the para-position is already substituted by another group. These investigations should also throw some light on the method of degradation of the nitrogenous side-chain. The substances investigated with this object were *p*-chlorophenylalanine and *p*-chlorophenylpyruvic acid, both of which were excreted with glycine in the form of *p*-chlorophenylaceturic acid,

$$C_6H_4Cl\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H.$$

The corresponding hydroxy-acid, *p*-chlorophenyl-lactic acid, was not excreted in this form, and the results indicate that amino-acids are broken down in the body with deamidisation into an acid with one carbon atom less, and that the corresponding α-hydroxy-acids are not formed as intermediate products.

p-Chlorophenylalanine was prepared by condensing *p*-chlorobenzaldehyde with hippuric acid to form the *lactimide* of p-*chloro-α-benzoylaminocinnamic acid*, $C_6H_4Cl\cdot CH{:}C{<}{\substack{NH\cdot CO\cdot C_6H_5 \\ | \\ CO}}$ (m. p. 195°), which on hydrolysis yielded p-*chloro-α-benzoylaminocinnamic acid* (m. p. 216°); this was reduced by sodium amalgam to *benzoyl*-p-*chlorophenylalanine* (m. p. 171—172°), which on treatment with hydrochloric acid yielded the *hydrochloride* of p-*chlorophenylalanine*. From this the free *amino-acid* (m. p. 243—244°) was obtained.

p-*Chlorophenyl-lactic acid* (m. p. 85—87°) was obtained from the above by the action of nitrous acid.

p-*Chlorophenylpyruvic acid* (m. p. 191°, decomp.) was obtained by the action of sodium hydroxide on *p*-chloro-α-benzoylaminocinnamic acid.

p-*Chlorophenylaceturic acid* (m. p. 165°) was synthesised by the action of *p*-chlorophenylacetyl chloride (b. p. 120°/14 mm.) on glycine in presence of sodium hydroxide. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. X. The Behaviour of αβ-Dihydroxy-acids in the Animal Body. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, 27, 113—118).—As both saturated and unsaturated acids yield the same products in the animal body, and as β-ketonic acids are supposed in both cases to be intermediate products, experiments were carried out with αβ-dihydroxy-acids to determine whether such acids were also intermediate products in the degradation of acids, and whether they also yield keto-acids, and are formed as the first stage in the degradation of the unsaturated acids. Perfusion experiments with αβ-dihydroxybutyric acid yielded no acetoacetic acid on perfusion, neither did phenylglyceric acid after ingestion yield acetophenone (or benzoylacetic acid). These results indicate that the dihydroxy-acids are not formed as intermediate metabolism products, and that probably, by addition of water at the double bond, β-hydroxy-acids are first formed, which oxidise to keto-acids. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XI. The Behaviour of Benzoylacetic Acid in the Animal Body. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1910, 27, 119—130).—In view of the conceptions advanced by Knoop and by Dakin as to the formation of β-hydroxy-acids as intermediate products in the degradation of acids in the animal body, and in view also of the fact that phenylpropionic acid entirely disappears after administration to animals, whereas the supposed intermediate product, β-hydroxyphenylpropionic acid, does not, experiments were carried out with the other possible intermediate product, namely, benzoylacetic acid. The following products were obtained in the urine when this substance was administered subcutaneously to dogs in doses of 0·35 gram per kilo. of body-weight: *l*-β-hydroxyphenylpropionic acid, acetophenone, cinnamoylglycine, and hippuric acid. The author represents the changes by the following scheme:

$$\begin{array}{ccc}
C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO_2H & \rightleftarrows & C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \\
\downarrow & & \downarrow\uparrow \\
C_6H_5{\cdot}CO_2H & & C_6H_5{\cdot}CH{:}CH{\cdot}CO_2H \\
 & & \downarrow \\
 & & C_6H_5{\cdot}CO_2H
\end{array}$$

From these results, and from those of other authors, it would appear that certain of the changes are reversible. S. B. S.

Mode of Oxidation of Phenyl Derivatives of Fatty Acids in the Animal Organism. A Correction. HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 8, 35—39).—The substance previously in-

vestigated (Abstr., 1909, ii, 685), and supposed to be phenyl-β-alanine, turns out, as Posner showed, to be the amide of β-hydroxyphenylpropionic acid. Pure phenyl-β-alanine was prepared by Posner's method, and given to dogs and cats either by the mouth or subcutaneously. The urine contains much of the unchanged acid; on concentration on the water-bath it reacts with carbamide to form β-carbaminophenylpropionic acid, and this by the subsequent action of acids in the course of the analysis may be converted into the corresponding anhydride, phenyldihydrouracil. No indications of the formation of β-hydroxyphenylpropionic acid, acetophenone, or hippuric acid were found, so contrasting with the corresponding hydroxy- and ketonic acids, both of which are converted into hippuric acid. W. D. H.

Mode of Decomposition of Tyrosine and of Related Substances in the Animal Body. Henry D. Dakin (*J. Biol. Chem.*, 1910, 8, 11—24).—The experiments failed to demonstrate in normal animals the type of change necessary for the conversion of tyrosine or phenylalanine into homogentisic acid. The inference that the latter acid is not a normal product of catabolism is, however, still inconclusive. Jaffé found muconic acid in the urine of dogs after dosage with benzene; this suggests that the oxidation of the aromatic nucleus in phenylalanine and tyrosine may not necessarily be preceded by the introduction of hydroxyl groups into the ring. The frequent occurrence of the $CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ grouping in amino-acids, which undergo complete decomposition in the body, is significant. The group readily undergoes condensation with other amino-acid groupings in the tissues, and this may be a necessary preliminary to the oxidation of aromatic nuclei. The fact that phenylaminobutyric acid undergoes easy oxidation in the body and in alcaptonuria is not converted into an alcaptan acid, harmonises with this view, as also do certain other facts which are quoted. W. D. H.

Fate of Inactive Tyrosine in the Animal Body, together with some Observations on the Detection of Tyrosine and its Derivatives in the Urine. The Synthesis and Probable Mode of Formation of Blendermann's *p*-Hydroxybenzylhydantoin. Henry D. Dakin (*J. Biol. Chem.*, 1910, 8, 25—33).—Inactive tyrosine administered to cats undergoes selective decomposition, so that the tyrosine of the urine contains more of the dextro- than of the naturally-occurring lævo-variety. When neutral or alkaline urine which contains tyrosine is evaporated, the tyrosine is largely converted with the corresponding uramino-acid. On subsequent treatment with acids, this readily loses water, giving the hydantoin derivative, *p*-hydroxybenzylhydantoin,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{<}\begin{matrix}NH{\cdot}CO{\cdot}NH_2\\CO_2H\end{matrix} \longrightarrow OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{<}\begin{matrix}NH{\cdot}CO\\CO{-}NH\end{matrix},$$

described by Blendermann in the urine of rabbits dosed with tyrosine. Blendermann's substance is no doubt the result of analytical procedure. It is important to avoid heating the urine unless it is acidified. No homogentisic or similar acid was found. W. D. H.

Action of Nicotine and Curare on the Receptive Substance of the Frog's Rectus Abdominis Muscle. Antagonism by Curare of the Nicotine Stimulation of Nerve Cells. JOHN N. LANGLEY (*Proc. physiol. Soc.*, 1910, lix—lx, lxii; *J. Physiol.*, 40).—Further experiments are described which support the view that curare combines with the receptive substance and can be displaced by nicotine. This antagonistic action is fundamentally the same on autonomic nerve cells and on striated muscle. W. D. H.

[Physiological] Action of Tetrahydropapaveroline. P. P. LAIDLAW (*J. Physiol.*; 1910, **40**, 480—491).—Tetrahydropapaveroline hydrochloride was first prepared by Pyman (Trans., 1909, **95**, 1610), during his study of the reduction products of papaverine. It causes a fall of blood pressure, although the heart rate is increased; the fall is due to vascular dilatation; the respiration rate is augmented, and the plain muscle of the bronchioles is completely relaxed; the same is true for the arteries and, to a less extent, for the intestine; the bladder and skeletal muscle are not affected. W. D. H.

[Physiological] Action of Kamala and its Constituents. AUG. SEMPER (*Arch. exp. Path. Pharm.*, 1910, **63**, 10—37).—This anthelmintic is toxic to frogs, tadpoles, and worms. The symptoms produced in frogs are similar to those resulting from different *Filix* substances; the same similarity is seen in its action on muscle and nerve. The action of rottlerin, a substance obtained from kamala, and the ethereal extract show the same action in smaller degree. In dogs, kamala and its products are not absorbed, unless their use is prolonged, and then local changes in the intestine and albuminuria occur. W. D. H.

Certain Bases which Occur in the Urine During Phosphorus Poisoning. K. TAKEDA (*Pflüger's Archiv*, 1910, **133**, 365—396).—On the hypothesis that oxidation is lessened in the body in phosphorus poisoning, the urine of five dogs poisoned with that substance was examined for abnormal bases. The urine contained a trace of protein, but no sugar, leucine, or tyrosine. In all, 65 litres of urine were collected. After acidification with sulphuric acid, phosphotungstic acid was added. By fractional treatment of this precipitate with silver nitrate and mercuric chloride, compounds of certain bases were obtained, in some cases in crystalline form. The identification of these bases was incomplete; one appears to be isomeric with crangonine ($C_{13}H_{26}O_5N_2$), a base separated from crab extract by Kutscher and Ackermann, and another with Brieger's base, $C_7H_{15}O_2N$, prepared from putrefying material. These are toxic, acting mainly on the heart, and lowering arterial pressure. Other bases somewhat similar to histidine and pyrimidine bases were found, but not identified; one suspected to be butyrobetaine gave an intense odour of trimethylamine when destroyed. W. D. H.

Thyroidectomy and the Resistance of Rats to Morphine Poisoning. W. H. OLDS, jun. (*Amer. J. Physiol.*, 1910, **26**, 354—360).—Rats survive thyroidectomy without harm, provided the

recurrent laryngeal nerves are intact and the parathyroids not entirely removed. They show the same resistance to morphine poisoning as normal rats. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Rôle of Methane in Organic Life. N. L. SÖHNGEN (*Rec. trav. chim.*, 1910, [ii], **14**, 238—274. Compare Hoppe-Seyler, Abstr., 1886, 577, 932).—The observations of Omelianski (Abstr, 1902, ii, 468) relating to the fermentation of cellulose are confirmed.

The author has studied the fermentation of the calcium salts of fatty acids first observed by Hoppe-Seyler (Abstr., 1887, 618, 1135; compare also Mazé, Abstr., 1904, ii, 138; Pakes and Jollyman, Proc., 1901, **17**, 29). If a quantity of sewer or canal mud (40 c.c.) is mixed with a solution (100 c.c.) containing 0·05% of dipotassium hydrogen phosphate, 0·05% of ammonium chloride, and 2% of a calcium salt of a fatty acid, and the mixture kept at 35°, a vigorous fermentation takes place. After several repetitions of the process, the residue becomes quite white, probably from the destruction of humus and formation of calcium carbonate. The active micro-organism is present only in the sediment, not in the supernatant liquor; the former, after repeated cultivation, is found to contain a bacterium and a sarcina, both of which ferment fatty acids. The bacterium takes the form of a small rod, 5—7 μ long and 0·3—0·5 μ wide; it is largely enveloped by the calcium carbonate, and predominates in cultures other than those of calcium acetate. The sarcina is rather larger, but less active, than the bacterium, and predominates in acetate cultures. Neither organism forms spores, both are killed at $\pm$ 60°, are active only in neutral liquids, and are stained by aniline dyes. The sarcina resists drying at 40°, whilst the bacterium is destroyed, and separation can be effected by this means. The activity of the bacterium is lessened by increasing the concentration of the salt of the fatty acid, and is inhibited when this amounts to 10%. This bacterium does not ferment cellulose. Experiments are described in which a culture residue, prepared as above, was treated with solutions of calcium butyrate and formate. The results of these show that the butyrate is fermented according to the equation: $Ca(C_4H_7O_2)_2 + 3H_2O = 5CH_4 + 2CO_2 + CaCO_3$, and the formate according to $2Ca(CHO_2)_2 = CH_4 + CO_2 + 2CaCO_3$. The calcium salts of other acids containing an even number of carbon atoms are decomposed by similar reactions. Acids containing an odd number of carbon atoms, except formic acid, are not attacked.

When the pure culture of Omelianski's methane-forming bacillus, obtained by repeated cultivation with pasteurisation of a dung-culture, is inoculated in a sterile solution of mineral salts containing filter paper and calcium carbonate, and placed in an atmosphere of hydrogen, the latter gradually disappears, whilst methane and carbon dioxide are evolved.

Similarly, if a solution of calcium butyrate in a hydrogen atmosphere is inoculated with the sediment of a culture of the acid-fermenting organism, the hydrogen is absorbed, whilst methane and carbon dioxide are liberated. More hydrogen, however, is absorbed, and less of the other gases liberated, than is required by the equation :

$$Ca(C_4H_7O_2)_2 + 4H_2 + H_2O = 6CH_4 + CO_2 + CaCO_3.$$

A similar discrepancy is observed in experiments with calcium formate. This discrepancy is explained by the observation that carbon dioxide (from the calcium hydrogen carbonate present in the culture) under the influence of the organism is reduced by hydrogen to methane. Thus a mixture of 1350 c.c. of hydrogen and 300 c.c. of carbon dioxide, confined at 35° under pressure in a vessel containing a solution of mineral salts and a culture of the acid-fermenting bacterium, diminished in eighteen days to 444 c.c., composed of 159 c.c. of hydrogen and 285 c.c. of methane, in accordance with the equation: $CO_2 + 4H_2 = CH_4 + 2H_2O$.

The paper ends with an account of work on the *Bacillus methanicus*, already published (Abstr., 1906, ii, 42). E. H.

Biochemistry of Micro-organisms. III. The Fermentation of Formic Acid by the Bacillus phymonthiensis. HARTWIG FRANZEN and G. GREVE (*Zeitsch. physiol. Chem.*, 1910, **67**, 251—296. Compare this vol., ii, 333).—Further details regarding the fermentation of formic acid are given in reference to varying conditions of temperature, etc. Two strains of the *B. phymonthiensis* (*K. G.-A.* and *Kràl*), although morphologically so much alike, differ in their relative action in this direction. W. D. H.

A Chemically Characterised Hæmolysis of Bacterial Origin, Hydroxythioldimethylerucic Acid, the Hæmolysin of Bacterium Putidum (Lehmann and Neumann). LUDWIG BURKHARDT (*Arch. exp. Path. Pharm.*, 1910, **63**, 107—118).—The substance produced by *B. putidum* which acts as a hæmolysin is a monobasic unsaturated acid, which was identified as *hydroxythioldimethylerucic acid*, $C_{24}H_{46}O_2S$, probably $OH\cdot C_{21}H_{41}Me_2\cdot CO\cdot SH$. Several of its salts were prepared ; on oxidation it yields dihydroxybehenic acid; whether immunisation against it can be produced has not yet been attempted. W. D. H.

Oxidation of Acetaldehyde by Lower Vegetation. A. PERRIER (*Compt. rend.*, 1910, **151**, 163—165).—A species of *Torula* was cultivated in a medium containing definite amounts of acetaldehyde, but free from other organic substances. Progressive disappearance of aldehyde was observed, but no products of incomplete oxidation were detected. Negative results were obtained in similar experiments with formaldehyde. The results confirm the theory that alcohol and aldehyde are two successive stages in the degradation of sugars by micro-organisms. W. O. W.

The Dependence of Plant Respiration on the Presence of Lipoids. WLADIMIR PALLADIN and E. STANEWITSCH (*Biochem. Zeitsch.*, 1910, **26**, 351—369).—Wheat embryos were extracted with different organic solvents, and then soaked for a short time in water.

The amount of carbon dioxide evolved during definite intervals was then estimated. It was found that those solvents which extracted the most lipoid substance and phosphorus depressed most the respiration energy. In order to obtain killed plants with the most active ferments, it is needful to employ substances in which the lipoids are least soluble. Toluene vapour exerts an injurious effect on the carbon dioxide excretion of plants; the toxicity varies with the nature of the solvent which had been employed for the extraction of the seedlings.

S. B. S.

Vegetable Assimilation and Respiration. VI. Some Experiments on Assimilation in the Open Air. D. Thoday (*Proc. Roy. Soc.*, 1910, *B*, **82**, 421—450).—Nothwithstanding the low concentration of carbon dioxide in the air, high rates of assimilation occur. Leaves of *Helianthus annuus* showed an average net rate of increase of 17 mg. per hour in their dry weight per square dcm., a result agreeing closely with that obtained by Sachs (16·5 mg.). It is probable that when the stomata allow sufficient carbon dioxide for this assimilation to diffuse into the leaf, the internal leaf-temperature will be the limiting factor unless it exceeds 23—25°.

The high results obtained with *H. annuus* indicate that the waste of available energy on a bright day has been over-estimated. On sunny days the waste is probably about 70%, and sometimes less.

The low results obtained by Brown and Escombe (5·5 mg.) are attributed partly to the unnaturally high temperatures in the glass leaf-cases employed; and it is probable that the stomata were not fully open. It is suggested that the failure of even very bright diffused light fully to open the stomata of *H. annuus* depends, not on the photosynthetic value of the radiation, but on the relative poverty in heat rays.

Whilst attached leaves have to absorb water from the stem against a negative pressure, the resistance has no longer to be overcome when the leaves are detached, and such leaves may be expected to open their stomata more widely than similar leaves still on the plant.

N. H. J. M.

The Behaviour of Nuclein Bases in the Dark in Plants. Alexander Kiesel (*Zeitsch. physiol. Chem.*, 1910, **67**, 241—250).—Although the nuclein bases in plants are so similar to those in animals, uric acid has never be found in the vegetable kingdom. In the dark, deamidation takes place, and xanthine and hypoxanthine increase at first, whilst adenine and guanine disappear. Later, the two former bases also diminish. There is no trace of uric acid found. Whether allantoin is formed has still to be discovered. W. D. H.

Chemical Examination of the Oil from the Seeds of Bursaria spinosa (Blackthorn). Edward Griffiths (*J. Roy. Soc., New South Wales*, 1909, **43**, 399—405).—The seeds of *Bursaria spinosa* yield by extraction with light petroleum about 17% of a yellow, transparent oil having the following constants: saponification number, 169·47; iodine number (Hübl), 86·4; D^{15° 0·8867; acid

number, 1·26 ; n_D^{21} 1·4681. The oil appears to consist mainly of olein with small quantities of stearin. Amongst the unsaponifiable constituents of the oil is a phytosterol and a wax-like substance, m. p. 45° (about). W. P. S.

Chemical Examination of the Rhizome of Cimicifuga racemosa. HORACE FINNEMORE (*Pharm. J.*, 1910, [iv], **31**, 142—144).—Forty kilograms of the dried rhizomes and roots of *Cimicifuga racemosa* have been extracted completely by alcohol in a Soxhlet apparatus. By boiling the concentrated alcoholic extract with water, a resinous precipitate is obtained. From the aqueous filtrate, *iso*-ferulic acid, a minute amount of salicylic acid and a crystalline *substance*, m. p. 152°, have been isolated. From the resinous precipitate, formic, acetic, butyric, and palmitic acids, oleic and other more unsaturated acids have been isolated, and also a *phytosterol*, $C_{20}H_{34}O$, m. p. 138°, an *alcohol* (?), $C_{15}H_{24}O_4$, m. p. 217—225°, and a *substance*, $C_{15}H_{24}O_4$, m. p. 218—220°.

Evidence has also been obtained of the presence of a small amount of alkaloids in the drug. C. S.

Fruit of Menispermum Canadense. RAY E. NEIDIG (*Chem. News*, 1910, **102**, 40—41).—The fruit is known under the name of "moon seeds," and is obtained from a vine growing to a height of about twelve feet. The berries are of a bluish-black colour, and resemble ordinary currants. They contain 61% of sugar, mainly dextrose, 5·38% of oil, 3·91% of ash, and 0·95% of nitrogen. The oil has D 0·9684, and is similar to castor oil; citric, oxalic, malic, and gallic acids are present in the fruits. W. P. S.

Toxicity of Certain Salts towards Green Leaves. LÉON MAQUENNE and EM DEMOUSSY (*Compt. rend.*, 1910, **151**, 178—182).—Observation of the blackening of leaves when immersed in salt solutions constitutes a simple method for determining the toxicity of substances towards protoplasm. In the case of copper sulphate, the reaction is very sensitive, the leaves showing a black border after twenty-four hours in a solution containing one part of copper in 5,000,000. Experimental data are given for various salts of the alkali metals and of ammonium, methylamine, and trimethylamine. Ammonium salts are much more toxic than those of potassium, sodium, or the two amines. W. O. W.

Physiological Action of Calcium Cyanamide, and Compounds Derived from it. FR. REIS (*Biochem Zeitsch.*, 1910, **25**. 477—493. Compare Abstr., 1910, i, 465).—Cyanamide, the active and important constituent of the commercial calcium cyanamide, is a powerful poison. It acts destructively, not only on animals, but on bacteria, moulds, germinating seeds, and also on growing plants, if it constitutes the only source of nitrogenous nourishment. Certain organisms can, however, live in a 0·1 per cent. solution of this compound. Sterile earth has a direct decomposing action on cyanamide solution. Dicyanodiamide, dicyanodiamidine, and diguanide in

0·1 per cent. solution are also assimilated by certain organisms, but no liberation of ammonia has been observed under these conditions. Cyanamide is doubtless valuable as an artificial manure, and in order to learn under what conditions it loses its poisonous properties and becomes converted into a source of nitrogen utilisable by higher plants, experiments were carried out on plants in clean quartz sand. Similar experiments were made, using dicyanodiamide, dicyanodiamidine sulphate, and diguanide. If the soil was watered with the solution before sowing the seed, and no other available source of nitrogen was provided, the poisonous action was marked. If the plants had grown considerably before the compounds were added to the soil, dicyanodiamidine sulphate could be used to a limited extent, whilst dicyanodiamide and diguanidine sulphate could not be used as fertilisers.

When calcium cyanamide acts as a fertiliser, it undergoes some changes in the soil. These are not completely understood, but the formation of urea may play an important part, and it has been shown to be formed from calcium cyanamide in the presence of ferric oxide.

G. S. W.

Analytical Chemistry.

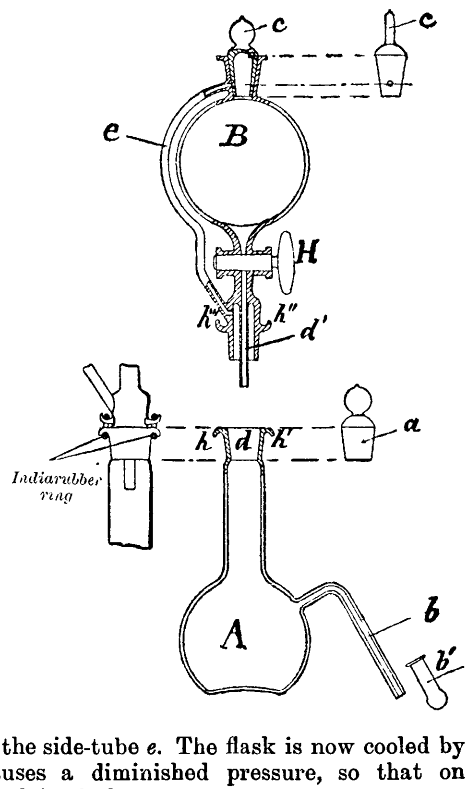
Use of Sodium Carbonate for Oxidising Purposes. EUGEN DEISS (*Chem. Zeit.*, 1910, 34, 781—782).—Sodium carbonate can be conveniently used for getting certain metals into a form in which they may be readily dissolved. The reaction takes place according to the equation $M + CO_2 \rightleftarrows MO + CO$, where M is a bivalent metal. For analytical purposes it is best to use a mixture of sodium carbonate with either lime or magnesia, so that the mass simply sinters together and allows the carbon monoxide to escape freely.

The mixture (2 parts of magnesia to 1 part of sodium carbonate, or 1 part of magnesia to 2 parts of sodium carbonate) may be used for transforming such difficult soluble substances as silicon, titanium, tungsten, molybdenum, ferro-titanium, manganese-titanium, ferro-phosphor, etc., into a soluble form. T. S. P.

Estimation of Sulphur in Pyrites; Roasted Pyrites and Sulphates. A. ZEHETMAYR (*Zeitsch. angew. Chem.*, 1910, 23, 1359—1360).—0·5 Gram of the finely-powdered substance is placed in a combustion tube, 60—70 mm. long and 7—8 mm. wide, and closed at one end, mixed by the aid of a wire with twice the weight of pure reduced iron, and the contents are heated for a short time to redness. When cooled somewhat, it is dropped into a 200 c.c. generating flask containing 20—30 c.c. of water, which will cause it to crack. The flask is then fitted in the usual manner with a safety funnel and a short condenser furnished with a tube bent at right angles dipping into dilute potassium hydroxide. The sulphide formed is then decomposed by hydrochloric acid, and towards the last the

solution is boiled to expel the last traces of hydrogen sulphide. The liquid in the receiver is then titrated for hydrogen sulphide by the ordinary iodometric method. L. DE K.

Estimation of Sulphur Trioxide in Fuming Sulphuric Acid. R. H. VERNON (*Chem. Zeit.*, 1910, **34**, 792).—The apparatus consists of two parts, a dilution flask *A* with ground stopper *a*, and side-tube *b* fitted with a ground cap *b'*, also a separating funnel *B*, with stopcock, and a side-tube *e*; this connects the part of the funnel below the stopcock *H* with the upper stopper *c*. This stopper is also ground and hollow, and provided with a hole which allows communication of the funnel with the side-tube *e*.



A fitted with *a* and *b'* is weighed, and by means of a rubber tube fixed in the neck *d*, and applying suction, about 10 to 15 grams of fuming sulphuric acid are introduced into *A*, *b* being immersed in the acid. After again closing the flask with the stopper and cap, *b* is rinsed with water and wiped dry, and by re-weighing *A*, the exact amount of the fuming acid taken is ascertained. *B* is now filled halfway with water, and *H* is turned until the tube *d'* is completely filled with water, and then again turned off. Air is now blown through the upper part of the funnel to expel the water from *e*; the upper stopper *c* is then inserted in such a manner that there is no communication between the funnel and the side-tube *e*. The flask is now cooled by streaming water, which causes a diminished pressure, so that on removing the stopper *a*, no sulphuric fumes can escape.

After placing *a* in a beaker containing water, the funnel *B* is inserted in *A* and held by means of indiarubber rings through the hooks *hh'*, *h''*, and *h'''*. The apparatus is now held in an inclined position, and *H* is carefully opened so as to allow one drop of water to fall on the side of the neck of *A*. Owing to the explosive action of the water on the fuming sulphuric acid, a super-pressure is caused. *A* is again cooled, and another drop of water is introduced. If the pressure is so great that no water will enter, the stopper *c* is turned so that there is a momentary communication between the upper and

lower part of the apparatus. The operation is now repeated until the acid is fairly well diluted; the funnel *B* is made to communicate with the flask *A* by turning *c*, and the remainder of the water is then admitted, at first slowly, finally rapidly. If sulphuric fumes are still visible in *B*, the apparatus is turned upside down, and the acid entering *B* soon absorbs the fumes on shaking. The funnel is then disconnected. In order to remove any acid from tube *b*, *b'* is slightly loosened, and *b* is then inserted in the beaker containing the stopper *a*, and *b'* is detached by means of a glass rod. Every part of the apparatus, including the beaker, is now rinsed, and the liquid finally made up to 1 litre, when 20 to 30 c.c. are taken from the usual titration.

The following formulæ will be found convenient in calculating the results. Total % sulphur trioxide = $80{\cdot}07 \times b \times f/aG = X$. Free sulphur trioxide = $X = 80{\cdot}07(100 - x)/18{\cdot}016$, in which b = c.c. of $N/5$-sodium hydroxide; f, factor of the lye; a, the weight of the fuming acid, and G, the number of c.c. of acid titrated. L. DE K.

Estimation of Nitrogen by Kjeldahl's Method in Fatty Substances. JOSEPH A. BROWN (*Chem. News*, 1910, **102**, 51).—When applying the Kjeldahl process to substances rich in fat, such as cheese or milk, traces of slightly volatile fatty acids may still be present at the end of the digestion with sulphuric acid, and when distilling off the ammonia after adding excess of alkali, a troublesome frothing may occur.

This difficulty is entirely overcome by adding to the contents of the Kjeldahl flask, 100 c.c. of water, and then boiling down briskly to about 40 c.c. The fatty acids are then completely expelled.

L. DE K.

Magnesium Ammonium Phosphate. KURT BUBE (*Zeitsch. anal. Chem.*, 1910, **49**, 525—596).—A lengthy paper containing a review of the investigations of Neubauer, Järvinen, Schmitz, Jörgensen, and others as to the best method of obtaining an ideal magnesium ammonium phosphate precipitate. This compound may be obtained with $1H_2O$ or $6H_2O$, but a mixture is frequently formed; this depends on the temperature.

Several tables and curves are given showing the solubility of the two compounds under various conditions, and the conductivity lines of the solutions.

The more important impurities which affect the analytical results are magnesium hydroxide, which is usually present when Jörgensen's directions are followed, and magnesium tetra-ammonium phosphate; this compound, the existence of which has been suspected by Neubauer, is, however, most likely magnesium ammonium phosphate, containing occluded ammonium phosphate.

The two crystallised compounds are decomposed by digestion with water at 47—48°; the decomposition is retarded when magnesium mixture has been added. L. DE K.

The Precipitation of Ammonium Phosphomolybdate in Presence of Organic Acids. G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 827—835).—Whilst the presence of tartaric or other

polybasic acids has sometimes been considered to hinder the precipitation of ammonium phosphomolybdate, other authors have recommended the addition of tartaric acid when it is required to precipitate phosphorus in the presence of much iron, as in the analysis of steel.

The two phosphate solutions employed were one of disodium phosphate in water and one of dicalcium phosphate in ammonium citrate, to which a little nitric acid had been added. To 10 c.c. of such a solution were added 30 c.c. of water, or 20 c.c. of water and 10 c.c. of a 34% solution of ammonium nitrate, followed by the organic acid, in quantity corresponding with that of the nitric acid usually added, and then, at a temperature near to boiling, variable quantities of solid ammonium molybdate. When this was dissolved, the precipitate was allowed to settle in the cold, and washed repeatedly with cold water in those experiments in which ammonium nitrate was not present, or with a solution of 5% ammonium nitrate and 4% nitric acid in other cases. The results are expressed in the form of tables and curves, and show that the presence of organic acids, glycerol, or sucrose does not hinder the precipitation if a sufficient quantity of nitric acid is present, and that organic acids may take the place of nitric acid, provided that a definite ratio of organic acid to precipitant is observed. Oxalic acid does not dissolve the phosphomolybdate except in hot concentrated solution, and then only with great difficulty, and tartaric acid in dilute solution is without influence. Fairly stable complex organic phosphomolybdic acids appear to exist. Sodium and calcium phosphates behave alike with respect to organic compounds. The results in the absence of ammonium nitrate are slightly low.

C. H. D.

The Aluminium Reaction of Mercury Salts Insoluble in Water. H. Hurt (*Pharm. Zentr.-h.*, 1910, **51**, 677—678).—A slight modification of Reichard's test (this vol., ii, 655) so as to make it applicable to mercury salts insoluble in water.

Mercurous chloride gives the reaction when placed on aluminium foil and moistened with a drop of ammonia; after pressing with a glass rod, the foil is rinsed and allowed to dry, when the characteristic spot will become visible.

Mercuric sulphide gives the same reaction when moistened with either aqueous sodium hydroxide or dilute hydrochloric acid.

L. de K.

A Method of Treating and Preserving Large Quantities of Urine for Inorganic Analysis. Edgar A. Slagle (*J. Biol. Chem.*, 1910, **8**, 77—79).—If sulphuric acid is added to the urine before evaporation, the residue dries hard without spirting, and can be removed from the dish (sometimes in a solid cake), and pulverised. This lends itself especially to estimation of inorganic constituents.

W. D. H.

Komarowsky's Colour Reaction. Th. von Fellenberg (*Chem. Zeit.*, 1910, **34**, 791—792).—According to Komarowsky (Abstr., 1903,

ii, 700), the "fusel" content of raw spirits may be estimated colorimetrically, as a red coloration is obtained on adding salicylaldehyde and sulphuric acid. According to the author, a similar reaction is obtained with the higher alcohols of the fatty series and their esters; also with the hydroaromatic alcohols, with phenols, and with those compounds which contain ethylene linkings in open chains or in hydroaromatic rings; tricyclic compounds, such as thujone, behave similarly. The exceptions are: the multivalent alcohols, the alcohols and phenols which contain carboxyl groups, the phenols which contain phenol groups in the ortho- or para-position, and the benzene derivatives with ethylene linkings which simultaneously contain a carboxyl group in the side-chain.

Brandy (cognac) is tested as follows: 10 c.c. of the distillate (obtained by rectifying the sample over potassium hydroxide and diluting the distillate to 30 vol.% alcoholic strength) are placed in a 100 c.c. flask, and 1 c.c. of a 1% alcoholic solution of salicylaldehyde is added; when much fusel oil is suspected, 5 c.c., diluted with 5 c.c. of 30% alcohol are added. Twenty c.c. of sulphuric acid are run down the side of the flask, and then mixed with the liquid by rotating gently. After forty-five minutes, 50 c.c. of 62% sulphuric acid are added, and the colour is compared with that of a liquid treated similarly and containing 2 parts of fusel oil in 1000 parts of 30 vol. % alcohol. L. DE K.

Gravimetric Estimation of Phenol. S. C. J. OLIVIER (*Rec. trav. chim.*, 1910, [ii], **14**, 293—295).—The alkaline solution of bromine, prepared for the estimation of phenol according to Mascarelli's directions (Abstr., 1909, ii, 353), contains sodium hypobromite as well as bromide and bromate.

When a solution of phenol at the ordinary temperature is treated with excess of a solution of sodium hypobromite, carbon tetrabromide is formed (compare Collie, Trans., 1894, **65**, 262), and the quantity of phenol found is only 22% of that calculated.

A comparison of estimations of phenol made with Mascarelli's solution and with a solution of sodium bromide (5 mols.) and bromate (1 mol.) shows that lower results are obtained with the former than with the latter solution, and that the difference is considerable when large amounts of the reagent are employed. The conclusion is drawn that Mascarelli's method becomes more accurate if his reagent is replaced by a solution of sodium bromide and bromate ($5NaBr + NaBrO_3$). E. H.

Carbohydrate Metabolism. I. A Colorimetric Method of Estimating Sugar, and its Results. LEONHARD WACKER (*Zeitsch. physiol. Chem.*, 1910, **67**, 197—218).—A colorimetric method is described, by means of which it is claimed that sugar can be accurately estimated (error, 0·01%) in such small quantities of fluid as 0·3 to 0·4 c.c. Percentages as low as 0·00005 can be estimated. The method can be used for clinical purposes in estimating the sugar in human blood, and the figures given for the amount of sugar in normal blood (and urine) are higher than those stated by previous observers. In the case of blood, protein is removed by iron alum and

sodium carbonate. To the filtrate, phenylhydrazine-*p*-sulphonic acid and sodium hydroxide are added, and the red colour is compared with a colour scale previously made with the same reagents and a standard solution of dextrose. By the use of the method, the disappearance of sugar in blood allowed to stand (glycolysis) can be estimated; the sugar in blood and urine rises normally after carbohydrate food. It rises in both if the animal (rabbit) is cooled, and this "cold diabetes" is regarded as a factor in heat regulation. W. D. H.

Influence of Iron on the Estimation of Glycogen. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, **27**, 53—60).—See this vol., ii, 792.

Test for Small Quantities of Cyanide. GEORG LOCKEMANN (*Ber.*, 1910, **43**, 2127—2128. Compare Berl and Delpy, this vol., ii, 661).—The substance to be tested is mixed with excess of dilute sulphuric acid and heated in a test-tube, the mouth of which is covered by a strip of filter paper (made by folding a piece of filter paper 1 dcm. square into a strip $2\frac{1}{2}$ cm. wide) which has been moistened with a drop of sodium or potassium hydroxide. The hydrogen cyanide liberated from the contents of the test-tube is absorbed by the alkali. After boiling for a short time, the paper is treated with a few drops of very dilute ferrous sulphate solution ($\frac{1}{4}$—$\frac{1}{2}$%), and allowed to remain in contact with the air for some minutes in order partly to oxidise the ferrous hydroxide to ferric hydroxide. The strip is then again steamed for a short time over the test-tube, and finally treated with a few drops of strong hydrochloric acid. The presence of cyanide is indicated by the formation of Prussian blue.

An alternative method of testing is to moisten the filter paper originally with alkali hydroxide and yellow ammonium sulphide. Thiocyanate is formed by the hydrogen cyanide liberated from the contents of the test-tube, and is tested for in the usual way by hydrochloric acid and ferric chloride.

The presence of 0·03—0·04 mg. of cyanogen in the form of potassium cyanide, and of 0·2—0·3 mg. in the form of potassium ferrocyanide, can be detected. T. S. P.

The Estimation of Lactic Acid by the Determination of the Amount of Acetaldehyde Obtainable by Scission Therefrom. OTTO VON FÜRTH and D. CHARNASS (*Biochem. Zeitsch.*, 1910, **26**, 199—220).—The authors have revised some of the previous work on the subject, and found that the volumetric method for estimating acetaldehyde by means of iodine and alkali (formation of iodoform and titration of excess of iodine) is untrustworthy, except under very special conditions, such as the preservation of great dilution and low temperature. The potassium hydrogen sulphite method of Ripper for the estimation of aldehydes gives, however, trustworthy results. The oxidative scission of the aldehyde from lactic acid does not proceed quite quantitatively; by keeping to certain standard conditions, employing a certain form of distillation apparatus, and keeping the sulphuric acid concentration low, a definite percentage

of the quantitative yield of aldehyde can be obtained. The authors give in detail the method that can be employed for obtaining trustworthy quantitative results. S. B. S.

Estimation of Methylamines in Presence of Large Quantities of Ammonia. JEAN BERTHEAUME (*Compt. rend.*, 1910, **151**, 146—149. Compare this vol., ii, 663).—The method already described for the estimation of mono-, di-, and tri-methylamine in presence of ammonia, not being applicable when the latter is in large excess, the author gives a modification based on Jarry's method for eliminating ammonia from mixtures of amines. Good results were obtained with a solution containing about 0·1% of the three methylamines in concentrated ammonia. W. O. W.

Detection of Hexamethylenetetramine and Formaldehyde in Wine. LÉON SURRE (*Ann. Falsif.*, 1910, **3**, 292—293).—The test proposed depends on the blue coloration produced when hexamethylenetetramine and codeine are heated together in the presence of sulphuric acid. From 100 to 200 c.c. of the wine are acidified with sulphuric acid (about six drops) and distilled; the distillate is treated with calcined magnesia and again distilled, in this case about 10 c.c. of distillate being collected in a receiver containing 1 c.c. of ammonia. Hexamethylenetetramine is thus re-formed, whether the wine contained this substance or formaldehyde. The ammoniacal solution (distillate) is evaporated under reduced pressure over sulphuric acid. The residue is then rinsed with a small quantity of water into a porcelain basin and evaporated to dryness on the water-bath. After cooling, a small fragment of codeine is crushed and mixed with the residue in the basin, and two drops of a mixture of 85 c.c. of sulphuric acid with 15 c.c. of water are added. A blue coloration appears after heating the basin and its contents on a water-bath for five seconds should the wine contain hexamethylenetetramine. The sulphuric acid employed must be free from iron, otherwise it will give a blue coloration with codeine alone. The test will detect as little as 2 mg. of hexamethylenetetramine in 1 litre of wine. W. P. S.

Differentiation of Iodine, Indican, and Scatole in Jaffé's Indican Reaction. BODO SPIETHOFF (*Chem. Zentr.*, 1910, ii, 45; from *Münch. med. Woch.*, 1910, **57**, 1066—1067).—The presence of indican or scatole in urine is a source of error in many iodine reactions, and, conversely, the presence of iodine interferes with the Jaffé test for scatole. The error is avoided when the liquid after shaking with chloroform is passed through a filter. The blue colouring matter is deposited on the filter, and, as these filters are permanent, a fair idea as to quantity present may be obtained by comparison experiments. If scatole is present besides iodine, the blue starch-iodine colour disappears on drying the filter; the red scatole deposit remains at the bottom of the filter. In the presence of indican, the filter remains blue on warming. L. DE K.

General and Physical Chemistry.

Lehmann's Anisotropic Liquids. GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.*, 1910, **151**, 327—329, 442—444).—A discussion of the optical properties of liquid crystals. The authors show that some of the phenomena exhibited by anisotropic liquids may be explained by regarding a thin layer of such a liquid as consisting of two films showing double refraction and enclosing a liquid having a very high rotatory power.

In the second paper, the authors discuss the appearances presented by Lehmann's liquid crystals when viewed under the microscope between nicol prisms, and arrive at the conclusion that these compounds are examples of a new state of matter entirely distinct from crystalline substances or isotropic liquids. W. O. W.

Optics of Liquid Crystals. ERNST DORN (*Physikal. Zeitsch.*, 1910, **11**, 777—780).—The refractive indices for both the ordinary and extraordinary rays have been measured in the case of the liquid crystalline substances, ethyl ethoxybenzylideneamino-α-methylcinnamate and ethyl ethoxybenzylideneamino-α-ethylcinnamate. Data were obtained for the wave-lengths $\lambda = 6708$, 5893, and 5461; for $\lambda = 5893$ determinations were made at different temperatures. The polarisation effects observed in the case of cholesteryl propionate are also described in detail. H. M. D.

Optical Investigation of an Optically Active Liquid Crystalline Substance. FELIX STUMPF (*Physikal. Zeitsch.*, 1910, **11**, 780—784).—Measurements of the refractive index for the ordinary and extraordinary rays have been made in the case of amyl *p*-cyanobenzylideneaminocinnamate. These show the magnitude of the dispersion and the influence of temperature on the refraction. The rotation of the plane of polarisation parallel to the optical axis, which is so markedly characteristic of liquid crystals, has also been examined in detail. The appearance of the substance under the ultra-microscope indicates that it is not homogeneous. H. M. D.

Molecular Refraction of the Isomeric Hydrocarbons, $C_{10}H_{22}$. PAUL ROHLAND (*Zeitsch. physikal. Chem.*, 1910, **74**, 382—384).—The isomeric hydrocarbons, *n*-decane, m. p. 173°, and di*iso*amyl, m. p. 163°, although they melt at different temperatures, have practically the same density and molecular refractivity. These facts are difficult to reconcile with the ordinary structure hypothesis, according to which a difference in constitution is associated with a difference in many physical properties. It is probable that the higher boiling point of *n*-decane is due to a certain degree of polymerisation. G. S.

Physical Properties of Binary Mixtures of Liquids. J. C. HUBBARD (*Zeitsch. physikal. Chem.*, 1910, **74**, 207—232).—The specific volumes at 25° and 35·17° or 50°, and the refractivities for the *C*, *D*, *F*,

and *G* lines of the following six binary mixtures—carbon disulphide–methylal, carbon disulphide–acetone, chloroform–acetone, ethyl iodide–ethyl acetate, acetic acid–benzene, and carbon tetrachloride–benzene—have been measured. Special precautions were taken in purifying the materials. In each case, mixtures containing varying proportions of the components were investigated. The choice of substances was determined by the fact that the partial pressures of binary mixtures containing them have already been measured by von Zawidzki (compare Abstr., 1901, ii, 6).

The variation of these properties (including the partial pressures) from the additive values are given in tabular form and are also represented graphically, the differences being plotted as ordinates against the composition of the mixtures as abscissæ. As regards the specific volumes, the deviations from additive behaviour increase in absolute value as the temperature rises. A rather doubtful exception to this rule is the chloroform–acetone mixture. Further, the deviation of the specific volume has the same sign in each case as that of the vapour pressure at the same temperature. The deviations of the refraction from the additive values have for the systems carbon disulphide–methylal, carbon disulphide–acetone, and carbon tetrachloride–benzene the same sign, and in the other cases the contrary sign, to the deviations of the vapour pressure and specific volume. The absolute values of the refractivity deviations increase as the wave-lengths diminish.

G. S.

Influence of Complex Formation on the Volume and Refractivity of Dissolved Substances. EBERHARD RIMBACH and R. WINTGEN (*Zeitsch. physikal. Chem.*, 1910, 74, 232—253).—The object of the investigation was to find if volume and refractivity measurements can be employed usefully to detect the formation of complexes between two substances in aqueous solution. It was, however, found that these methods are much less advantageous than those in general use.

For mixtures of certain salts, such as potassium and sodium chlorides, for which no complex formation is to be anticipated, the deviations from additive behaviour are less than the experimental error, and are very small even for mixtures of aluminium sulphate and alkali sulphates.

The deviations are noticeable, but are still comparatively small, for mixtures containing silver–potassium cyanide, mercuric potassium iodide, etc. As even these slight differences might be due to changes of ionisation, a number of experiments were made with isohydric mixtures of molybdic acid and other acids, both inorganic and organic. For mixtures containing phosphoric, arsenic, and iodic acid respectively, the deviations scarcely exceed the experimental error, although these substances are known to form complexes with molybdic acid. When organic acids which do not contain a hydroxyl group are used, the deviations in the case of refractivity are within the limits of experimental error, but are considerable for hydroxy-acids, corresponding with the fact that the latter form complexes with molybdic acid. No error arises in these measurements owing to a change in the molybdic

acid, as its molecular refractivity remains practically constant on dilution. The volume relations for the hydroxy-acids are rather less definite than the refractivity relations. G. S.

Long-waved Portion of the Banded Nitrogen Spectrum. REINER VON DER HELM (*Zeitsch. wiss. Photochem.*, 1910, **8**, 405—432).—To obtain information relating to the structure of banded spectra, the author has investigated the banded spectrum of nitrogen between $\lambda = 5000$ and $\lambda = 6900$. The wave-length measurements are discussed in detail with reference to the formulæ of Deslandres and Thiele. H. M. D.

Intensity Minimum of the Cyanogen Group of Bands, $\lambda = 3883 \cdot 558$. J. W. HAFERKAMP (*Zeitsch. wiss. Photochem.*, 1910, **9**, 19—36).—The influence of pressure on the distribution of the light intensity in the third group of bands in the cyanogen spectrum has been examined in detail. The observed variations are interpreted in terms of the electron theory. H. M. D.

Position of Ultimate Rays in Spectral Series. ANTOINE DE GRAMONT (*Compt. rend.*, 1910, **151**, 308—311. Compare Abstr., 1907, ii, 517).—Two types of spectra have been recognised in the study of the ultimate rays or lines of great persistence. In one, the lines do not fall into regular periodic series, but can be arranged in lines and parallel columns showing constant differences in wave-lengths, in this respect showing the regularities discovered by Kayser and Runge in the spectra of tin, lead, bismuth, antimony, and arsenic. The second type shows series converging to a finite limit. A principal series has been recognised in the ultimate rays for lithium, sodium, potassium, rubidium, and cæsium, but in the case of aluminium, indium, and thallium the principal series cannot be recognised; some of the lines for these metals appear to belong to a secondary series. Zinc, cadmium, and mercury show lines possibly belonging to an undiscovered principal series. W. O. W.

Emission and Absorption of Luminous Hydrogen. RUDOLF LADENBURG (*Ber. Deut. physikal. Ges.*, 1910, **12**, 549—564).—In part polemical against Pflüger (*ibid.*, 1910, **12**, 208). In reference to the relationship between the emission and absorptive capacity of luminous hydrogen, new measurements have been made which confirm the author's previous conclusion that the ratio of the emissive power to the absorptive power varies appreciably within the limits of the band H_a. H. M. D.

Spectra of the Metals in the Electric Arc. VIII. Spectrum of Uranium. B. HASSELBERG (*K. Svenska Vet-Akad. Handl.*, 1910, **45**, 3—69).—A detailed account is given of wave-length measurements in the arc spectrum of uranium from $\lambda = 3528$ to $\lambda = 5871$. The apparatus and the method were those previously used by the author in the investigation of the spectra of molybdenum (Abstr., 1903 ii, 706) and tungsten (Abstr., 1905, ii, 129).

From a comparison of the uranium and solar spectra, it is found that 75% of the principal uranium lines are absent from the solar spectrum.

On account of the very small intensity of the lines in the solar spectrum, which appear to coincide with the remaining uranium lines, the author considers that the actual coincidence is not established. The evidence points therefore to the absence of uranium in the sun.

H. M. D.

Uranium and Neodymium Aggregates. W. W. STRONG (*Physikal. Zeitsch.*, 1910, **11**, 668—671).—Observations are recorded showing the changes which occur in the absorption spectra of uranyl and neodymium salts when free acids are added to their aqueous solutions. The observations are interpreted in terms of the solvate theory, and it is supposed that the envelope of solvate molecules which surrounds the active nucleus may be of such dimensions that changes in the outer layers of the envelope have little influence on the absorption bands.

The bands in the spectra of uranyl salts are in no way similar to the bands furnished by uranous salts. The "water bands" and the "alcohol bands" of neodymium do not follow Beer's law, and the two series of bands are not affected in the same way by a change of temperature. H. M. D.

Anomalous Rotatory Dispersion. II. LEO TSCHUGAEFF and A. OGORODNIKOFF (*Zeitsch. physikal. Chem.*, 1910, **74**, 503—512).—In addition to the three compounds already referred to (compare Abstr., 1909, ii, 631), the following have now been found to show anomalous rotatory dispersion: methyl *l*-menthyl xanthate, $MeS{\cdot}CS{\cdot}O{\cdot}C_{10}H_{19}$; methyl, ethyl, and *n*-propyl *d*- and *l*-bornyl xanthates; *l*-menthylthiourethane, $CSPh{\cdot}NPh{\cdot}CO_2{\cdot}C_{10}H_{19}$; *l*-menthyl, *l*- and *d*-bornyl, and *l*-fenchyl dithiourethanes, $CSPh{\cdot}NPh{\cdot}CS{\cdot}OR$.

One of the objects of the investigation was to compare anomalous rotatory dispersion with the absorption of light. The latter was therefore also measured, but in the visible region only, with a König-Martens spectrophotometer. The results show that there is a close connexion between these two factors. The rotation curves for the methyl and ethyl esters of *l*-bornyl xanthate are very similar, as are the absorption curves, whilst for *l*-bornyl dixanthate both the rotation maximum and the absorption are displaced towards the red with reference to those for the two esters. Exactly corresponding results were obtained with the thiourethane derivatives. G. S.

Determination of the Optical Constants of Metals from Polarisation Measurements. W. VON ULJANIN (*Physikal. Zeitsch.*, 1910, **11**, 784—789).—Equations are deduced which give the relationship between the polarisation of the light reflected from metals and the optical constants. Measurements of the polarisation have been made in the case of mercury, nickel, and aluminium, and from these the refractive indices and extinction coefficients for red, yellow, and blue rays are calculated. It is shown that the polarisation effect is

only slightly influenced by considerable changes in the optical constants, but the author believes that this method of measurement should be of particular importance in the case of ultra-red rays.

H. M. D.

Ultra-violet Fluorescence and Chemical Constitution of Cyclic Compounds. HEINRICH LEY and K. VON ENGELHARDT (*Zeitsch. physikal. Chem.*, 1910, **74**, 1—64).—A more detailed account of work already published (compare Abstr., 1908, ii, 911). The vinyl and CH:C– groups, like the methoxyl and hydroxyl groups, act as auxofluors, and have also a strong bathofluor influence. From a qualitative point of view, the effect of two substituents in the benzene nucleus is additive, but there are certain exceptions in the case of unsaturated groups. Substitution in a saturated side-chain causes little or no spectral displacement of the benzene fluorescence, but when two unsaturated groups are attached to the same carbon atom, the results are anomalous.

G. S.

Simple and Combined Photochemical Reactions. ALFRED BENRATH (*Zeitsch. physikal. Chem.*, 1910, **74**, 115—124).—A purely photochemical reaction is one which does not proceed in the dark, and when exposed to light the rate is proportional to the amount of light energy absorbed. It follows that with constant illumination the rate of the reaction is proportional to the time of exposure. In a previous paper (compare Abstr., 1909, ii, 847) it has been shown that the reduction of ferric chloride by alcohols is a simple photochemical reaction, and the same is now shown to be the case when the reduction is affected by tartaric, citric, and oxalic acids and by glycerol. As before, a mercury vapour lamp was used as the source of illumination. The rate of reduction in quartz vessels is about double that in glass vessels, a result ascribed to the absorption of a considerable part of the light energy by the glass. The relative activities of malic, citric, lactic, tartaric, and mandelic acids as reducing agents are as 1 : 1·68 : 1·81 : 2·47 : 3·57. The reduction of ferric chloride by hydroxy-acids is much slower in acetone than in water.

A catalytic light reaction is one which proceeds slowly in the dark and is accelerated by light. It is shown, both by calculation of the results of Roloff (compare Abstr., 1894, ii, 221) on the oxidation of oxalic acid by bromine and by direct experiments with bromine and tartaric acid, that the reduction of Br_2 to $2Br'$ is a catalytic light reaction, as it proceeds more rapidly in light than in darkness, whilst the simultaneous reduction of Br_3' to $3Br'$ is a purely photochemical reaction. The whole process in this case may be termed a combined light reaction.

G. S.

Mechanism of Photochemical Reactions and the Formation of Vegetable Substances; Decomposition of Sugar Solutions. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **151**, 395—397. Compare this vol., i, 349, 543; ii, 564, 606).—This paper contains a discussion of results already published, and the results of analysis of the gaseous products obtained when sugar solutions are exposed to the light from a quartz-mercury lamp.

Carbon monoxide, carbon dioxide, methane, and hydrogen were obtained in each case. Dextrose gave equal volumes of carbon monoxide and methane with about six times as much hydrogen. Lævulose gave ten times as much carbon monoxide as methane. Maltose gave the same proportions as dextrose, whilst sucrose behaved as a mixture of dextrose and lævulose. W. O. W.

Photochemical Decomposition of Alcohols, Aldehydes, Acids, and Ketones. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, **151**, 478—481. Compare preceding abstract).—The results are given of analyses of the mixed gases obtained by exposing a number of substances to the action of light from a quartz-mercury lamp. The compounds examined included the first three members of the aliphatic saturated alcohols, aldehydes, and acids, also formamide and diethyl ketone. Acetone is decomposed very rapidly by ultra-violet light, giving carbon monoxide (49 vols.), methane (5 vols.), and ethane (46 vols.); in aqueous solution carbon dioxide is also formed. Solid calcium lactate gives the same gases with hydrogen; the proportion between this and the carbon dioxide is about the same as when these gases are produced in the butyric fermentation. Solid carbamide gives carbon dioxide, hydrogen, and methane; an aqueous solution evolves only the latter two, and becomes ammoniacal. W. O. W.

Chemical Changes Produced by Different Kinds of Rays. III. The Change of Benzoic Acid into Salicylic Acid in Sunlight. CARL NEUBERG (*Biochem. Zeitsch.*, 1910, **27**, 271—272. Compare Abstr., 1909, ii, 540).—If a solution of benzoic acid containing ferric chloride is exposed to sunlight, the violet colour characteristic for salicylic acid develops. Thirteen % of the benzoic acid was thus oxidised during sixteen days in June in Berlin. With ferrous sulphate the change of benzoic into salicylic acid also takes place, but it is slower. In artificial light the change can also take place. S. B. S.

Photoelectric Experiments with Anthracene. ALFRED BYK and H. BORCK (*Ber. Deut. physikal. Ges.*, 1910, **12**, 621—651).—Experiments are described which show that anthracene, although an insulator, is a photo-electrically active substance. This fact is connected with the observed photo-polymerisation of anthracene, and the action of light is supposed to consist in the removal of electrons, or in the splitting up of the neutral anthracene molecules into two oppositely-charged portions. H. M. D.

Tables of Constants of Ionisation and Radioactivity. T. H. LABY (*Le Radium*, 1910, **8**, 189—196).—These tables comprise values of (1) the coefficient of recombination, α, for different gases and its variation with pressure and temperature; (2) the coefficient of diffusion of ions produced by different agencies in different gases by the *X*-rays, and its variation with the pressure for ions produced by the β- and γ-rays; (3) the mobility of ions for air and various dry gases, and

the effect of temperature and pressure; and of the ions in non-conducting liquids and solids and in flames; (4) the ratio v_2/v_1 of the expansion necessary to produce condensation in gases and vapours ionised by *X*-rays and the rays of radium; (5) the charge *NE* of electrolytic and gaseous ions and of the ionic charge *e* as determined by various methods; (6) the number of molecules in a gram-molecule of gas; (7) the ratio ϵ/m of the negative electron as determined for cathode rays and secondary rays and from the Zeeman effect, and the variation of the ratio with velocity; (8) values of *RH*, the magnetic deviation, and *v*, the velocity of cathode rays; (9) ranges and velocities of α-rays, the number emitted from radium, the ratio ϵ/m of α-rays, the absorption in gases and metals, the number of ions produced by an α-particle, its variation with velocity, and the relative total ionisation in different gases (also for β-, γ-, and *X*-rays); (10) the disengagement of heat from radium, its emanation, and thorium; (11) the constant of the radium emanation, its volume, vapour pressure, and coefficient of diffusion; (12) radioactive and atomic constants.

F. S.

The Energy of the Rays of Radium. WILLIAM DUANE (*Compt. rend.*, 1910, **151**, 471—473).—A bolometer, radiometer, thermo-electric pile, and differential gas thermometer were all found unsatisfactory in showing the energy of the rays of radium, but results were obtained with the sensitive calorimeter previously described (Abstr., 1909, ii, 534). A tube containing the radium emanation was used as the source, and the rays passed through two thin mica windows, thin enough to allow the α-rays of radium-*C* to penetrate, but not those of the emanation or of radium-*A*. They fell upon the glass walls of an exhausted glass tube which was inserted into the calorimeter. A clear effect was produced which was stopped completely by two thin aluminium leaves. Hence the β- and γ-rays do not produce any appreciable effect. It is hoped in this way to obtain a measure of the energy of the α-rays throughout their range.

F S.

The β-Rays of Radium at its Minimum Activity. LÉON KOLOWRAT (*Compt. rend.*, 1910, **151**, 525—528).—The existence of a very absorbable β-radiation, specific to radium itself (Hahn and Meitner, Abstr., 1909, ii, 954), has been confirmed by new experiments. A small quantity of a radium salt was heated on a platinum plate, and its β-activity measured after different periods, and also the absorption coefficient of the β-rays by interposing a series of eight aluminium screens of graduated thickness. The value of the absorption coefficient μ rapidly decreased during the first few hours after heating from an initial value of about 200 (cm.)$^{-1}$ to a final value of 60. The value of the initial β activity, obtained by extrapolating the curves back to zero thickness, was about 2% of the final equilibrium β-activity. Hahn (with different measuring arrangements) had found it 7%, and for the value of μ 312 (cm.)$^{-1}$. The results are fully in accord with the hypothesis of the existence of a very absorbable β-radiation due to radium itself.

F. S.

The Disengagement of Heat in a Mixture of Radium and of a Phosphorescent Salt. WILLIAM DUANE (*Compt. rend.*, 1910, **151**, 379—381).—With the very sensitive calorimeter previously described (Abstr., 1909, ii, 534), a feeble development of heat has been detected from a phosphorescent salt one or two hours after it has been exposed to light. In most cases no effect is produced after twenty-four hours, but in others the development of heat persists even after the phosphorescence has become invisible. Experiments were made on the amount of heat developed from a preparation containing radium, alone and mixed with phosphorescent zinc sulphide. The heat evolution is proportional to the γ-activity of the preparation in each case, so that the presence of the phosphorescent salt is without effect. In other experiments the radium was contained in a sealed tube, and the β- and γ-rays allowed to produce phosphorescence in willemite or barium platinocyanide. The same development of heat was observed as when no phosphorescent salt was present. Hence there is no appreciable absorption or evolution of energy by the phosphorescent salt due to chemical reactions. F. S.

Radioactive Recoil Products (Projections). LOUIS WERTENSTEIN (*Compt. rend.*, 1910, **151**, 469—471. Compare this vol., ii, 476). —A disk of glass, rendered active by immersion in the radium emanation, was silvered in a silvering bath and dried. It was mounted opposite to a brass plate in a vacuum. It was found that a thickness of silver of the order of 10 $\mu\mu$ allowed about 60% of the recoil product to pass through, but a thickness of 20 $\mu\mu$ arrested it completely. The range of the recoiling particles was found to be about 0·7 mm. in hydrogen at atmospheric pressure, or six times the range in air, which is nearly the same ratio as is found for the range of the α-particle. The range of the recoiled particles or their number appears to diminish as the direction of emission from the surface becomes more oblique. A series of parallel disks charged alternately positively and negatively was placed in an exhausted vessel containing radium emanation and air at known low pressure. It was found that the active deposit on the positive plates increased rapidly with the distance apart of the plates up to a distance corresponding with the range of the recoiling particle, and then continued to increase about twenty times more slowly. This shows that recoil plays a part in the rendering active of surfaces by the emanation. Evidence of a strong ionisation produced by particles of radium-*D* recoiling from radium-*C* has been obtained. The total ionisation between two parallel plates, one coated with radium-*C*, increases rapidly with their distance apart up to the distance corresponding with the range of the recoiling particle, but further experiments are necessary to establish such an effect.
F. S.

Metallic Radium. Mme. MARIE CURIE and ANDRÉ DEBIERNE (*Compt. rend.*, 1910, **151**, 523—525).—Preliminary experiments with barium, using about 0·1 gram of material, by Guntz's method gave the necessary conditions and experience for the preparation of radium. The amalgam was obtained by electrolysis of a solution of 0·106 gram

of perfectly pure radium chloride with cathode of mercury (10 grams) and anode of platinum-iridium. After electrolysis, the solution contained 0·0085 gram of the salt. The amalgam was quite fluid, whereas with barium under similar conditions it is partly crystalline. The dried amalgam was transferred to an iron boat and heated cautiously in a quartz tube in a current of pure hydrogen, purified by passage through the walls of a platinum tube heated in an electric furnace. The temperature of the boat was determined by a thermo-couple. Most of the mercury was distilled at 270°. At 400° the amalgam became solid, and its melting point rose progressively as the mercury was driven off to 700°, when no more mercury volatilised, but the radium itself commenced to volatilise and to attack the quartz tube energetically. The boat now contained a brilliant white metal, fusing sharply in the neighbourhood of 700°, which was considered to be pure radium. It adhered strongly to the iron, and blackened immediately on exposure to the air, probably forming the nitride. A particle falling on white paper produced a blackening analogous to a burn. The metal decomposed water energetically, and dissolved for the most part, showing that the oxide is soluble. The small, black residue (? nitride) dissolved completely in a very little hydrochloric acid, showing that no mercury was present. The penetrating rays from the boat containing the metal, sealed in a glass tube, showed the normal increase following the law of production of the emanation. Owing to metallic radium being much more volatile than barium, it is proposed to purify it by sublimation in a vacuum. F. S.

Radio-Lead. H. Herchfinkel (*Le Radium*, 1910, 8, 198—200).—Numerous unsuccessful attempts to concentrate the radium-*D* in radio-lead are described. The raw material is lead nitrate of an activity three to four times that of uranium oxide. Various metals were immersed in the solution. The chloride and bromide were fractionally crystallised. Cerium nitrate was precipitated in the nitric acid solution. Iron was precipitated in the solution as the basic acetate, and again barium sulphate by addition of barium nitrate and sulphuric acid. Digestion of the solution with animal charcoal, excepting one case which could not be repeated, resulted in no concentration of the radium-*D*. The active metallic lead was distilled at 600—700°, but the portion volatilising was not permanently active. Possibly a concentration in the non-volatile part might be effected in this way. A few per cent. of zinc was added to the lead and distilled off at about 1250°, and the distillate possessed a constant activity a little greater than the initial substance. A triple alloy of zinc and silver formed with the lead contained only polonium. No successful method of concentration was found. F. S.

Occurrence of Free Electrons in Chemically Inert Gases at Atmospheric Pressure. J. Franck (*Ber. Deut. physikal. Ges.*, 1910, 12, 613—620).—Measurements of the velocity of the negative ions in chemically pure argon and nitrogen indicate the presence of free electrons. If small quantities of oxygen are mixed with these inert gases, the mobility of the negative ions is reduced to about 1% of

its value in the pure gases. The addition of chlorine, water or nitric oxide causes a similar reduction in the ionic mobility, and it is supposed that these substances combine with the free electrons and thus yield negative ions which are much less mobile than the free electrons. H. M. D.

Decomposition of Water Vapour by the Silent Electrical Discharge. MIROSLAW KERNBAUM (*Compt. rend.*, 1910, **151**, 319—322. Compare Abstr., 1909, ii, 364, 714, 717).—A brush discharge was made to play in an atmosphere of water vapour free from air. Hydrogen and hydrogen peroxide were produced, probably in accordance with the equation $2H_2O \rightleftharpoons H_2O_2 + H_2$. The amount of hydrogen obtained depends largely on the condition of the platinum electrode, a new point giving 2·4% in the first experiment, 0·8% in a second, and practically none in a third. The results are analogous with those obtained in the action of ultra-violet light and the β-rays of radium on water, and appear to be due to ionisation produced by cathode radiation. W. O. W.

Conduction of Electricity in Crystals at High Temperatures. CORNELIO DOELTER (*Monatsh.*, 1910, **31**, 493—555. Compare Abstr., 1906, ii, 665; 1908, ii, 178, 839; Kœnigsberger, Abstr., 1909, ii, 289).—Electrolytic as well as metallic conduction can occur in crystals. The conductivity temperature curves are not sufficient to distinguish between the two types of conductivity; determinations of polarisation are essential. As a result of examination of these two properties, substances are divided into three classes: 1. Crystals which give no polarisation and in which the conductivity increases with the temperature. To this group belong rutile, tinstone, chrysoberyl, and probably wolframite. 2. Substances which show slight polarising effects at very high temperatures; for example, adularia and albite. 3. Crystals which show appreciable polarisation at high temperatures; for example, sapphire, barytes, topaz. In these cases the conductivity diminishes as the temperature rises.

The most trustworthy conclusions can be drawn by determining both resistance and polarisation at temperatures until the mass is quite molten.

In the case of silicates, the polarisation is small even in the fused state (for example, only a few tenths of a volt), and this is accompanied by a high resistance which is attributed to the high viscosity rather than to low dissociation. The conductivity becomes greater at temperatures much above the melting point. The conductivity of albite, in spite of its high viscosity, is some ten times as large as that of labradorite at a temperature of 1200—1300°. The ratio of conductivities of albite solid at 1000° and albite liquid at 1250° is 1 : 2, and the curve, using the Kohlrausch-Arrhenius method, for the transition solid to liquid is a straight line.

Electron conductivity is possible in the liquid state, and probably many sulphides, sulphonic acids, and antimonite behave in this way.

Difficulties are met with in the case of quartz; many specimens show high conductivities, but this is due to secondary causes, as in some

cases it has been found possible to obtain a metal (sodium) by electrolysis.

The following division of crystals is given: *A*. Those which exhibit metallic conductivity at all temperatures without electrolytic conductivity—lead sulphide, antimony sulphide, ilmenite, pyrites, and magnetite.

B. Crystals which are insulators at the ordinary temperature, but which exhibit metallic conductivity at rather higher temperatures; for example, zinc blende, molybdenum sulphide, pyrites, antimony pyrites, fahlore. *C*. Crystals, such as tinstone and chrysoberyl, in which polarisation has not been definitely determined, but which probably exhibit both metallic and electrolytic conductivity. *D*. Crystals which are insulators at the ordinary temperature, but are conductors at high temperatures and show appreciable polarisation; for example, metallic chlorides and iodides, barium sulphate, sapphire, and silicates.

The transition from the amorphous to the crystalline state is usually accompanied by a break in the temperature conductivity curve.

In the case of polymorphous substances, the form which is the more stable at high temperatures has the greater conductivity.

J. J. S.

Abnormal Action of the Gas Electrode in the Determination of the Concentration of Hydrogen Ions by Electric Measurement. J. E. ENKLAAR (*Chem. Weekblad*, 1910, 7, 733—735).—The results obtained when the concentration of the hydrogen ions in a solution of chloral hydrate containing a neutral salt is determined are abnormal, and comparable with those furnished by a strong mineral acid. The author attributes this abnormality to displacement of chlorine by hydrogen, with formation of acetaldehyde and hydrochloric acid.

A. J. W.

Hydrolysis of Iodine and of Bromine. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1910, **32**, 932—938).—The work described in this paper was carried out in order to ascertain the cause of the conductivity of aqueous solutions of iodine. From calculations based on Sammet's determinations of the equilibrium constants (Abstr., 1906, ii, 153), the conclusion was drawn that both the following reactions must be considered: (1) $I_2 + H_2O = H^+ + I^- + HIO$, and (2) $3I_2 + 3H_2O = 6H^+ + 5I^- + IO_3^-$. It was expected that the conductivity would at first rise rapidly in accordance with (1) and then continue to rise slowly in accordance with (2), and this has been confirmed.

Determinations have been made of the solubility of iodine and bromine in water, and of the conductivity of the solutions at 25°. The results show that iodine is soluble to the extent of 1·32 millimols. I_2 per litre, and bromine to the extent of 0·21 mol. Br_2 per litre. The hydrolysis constants: $(H^+)(I^-)(HIO)/(I_2)$ and $(H^+)(Br^-)(HBrO)/(Br_2)$ have been found to be $0·6 \times 10^{-12}$ and $2·4 \times 10^{-8}$ respectively.

E. G.

Conductivity and Ionisation of Potassium Tri-iodide, and the Equilibrium between Iodine, Iodide, and Polyiodides in Aqueous Solution. WILLIAM C. BRAY and G. M. J. MACKAY (*J. Amer. Chem. Soc*, 1910, **32**, 914—932).—This investigation was carried out with the object of determining the equivalent conductivity of the tri-iodide ion, I_3^-, a knowledge of which is required in the study of the equilibrium between iodine, potassium iodide, and polyiodides in aqueous solution. The conductivities of potassium iodide solutions of concentration between $0·1N$ and $0·001N$, and of the same solutions saturated with iodine have been determined at 25°.

The results show that the degree of ionisation of potassium tri-iodide in dilute solutions is practically identical with that of potassium iodide up to a concentration of $0·1N$, and that the values of Λ_I and Λ_{I_3} at 25° are 76·5 and 41·0 respectively, that of potassium iodide being regarded as 74·8. Burgess and Chapman (Trans., 1904, **85**, 1305) found by means of transference experiments that $\Lambda_{I_3}/\Lambda_I = 0·566$, whence if Λ_I is taken as 76·5, Λ_{I_3} has the value 42·5. An intermediate value, 41·5, has therefore been adopted as the most probable value of Λ_{I_3}. It has also been found that in potassium iodide solutions saturated with iodine the ratio $C_{I^-}/C_{I_3^-}$, which, according to the law of mass action, should be a constant, decreases from 1·16 to 0·99 between $0·0N$ and $0·1N$; the effect due to the presence of potassium iodide, which is known to occur in more concentrated solutions, is therefore apparent also in very dilute solutions.

An attempt has been made to determine the composition of concentrated solutions of potassium iodide saturated with iodine. An exact solution of the problem is not possible, but it appears that the ratio of "activity" (Lewis, Abstr., 1908, ii, 16) to concentration for the iodide ion is nearly independent of the concentration, that this ratio for the tri-iodide ion decreases rapidly in concentrated solutions, and that higher polyiodide ions show this abnormality in a still higher degree. In a N-solution of potassium iodide, saturated with iodine, the concentration of KI_5 is calculated to be about 0·08 molal if this is the only higher polyiodide present. E. G.

Conductivity of Some Concentrated Aqueous Solutions at Zero. W. H. SLOAN (*J. Amer. Chem. Soc.*, 1910, **32**, 946—949).—On determining the conductivity of concentrated aqueous solutions of potassium iodide at 0°, unexpected values were obtained. These results have been confirmed, and the conductivities of concentrated solutions of potassium bromide, sodium nitrate, ammonium nitrate, silver nitrate, and cupric nitrate have also been determined. The results are tabulated and plotted as curves.

The values obtained with potassium iodide differ from those found by Jones and Douglas (Abstr., 1902, ii, 59), but the type of curve agrees closely with that of Kahlenberg (Abstr., 1901, ii, 540). The values resemble in some respects those obtained for certain salts in methylamine and liquid ammonia (Franklin and Gibbs, Abstr., 1907, ii, 840; Franklin, Abstr., 1909, ii, 957).

The conductivity of the potassium bromide solutions resembles that of the potassium iodide solutions, but the limited solubility of the

former salt excluded the possibility of examining very concentrated solutions. The other salts did not give any exceptional values except in the case of cupric nitrate, in which the specific conductivity increased up to a certain point with the dilution and then diminished.

E. G.

Conductivity and Dissociation of Organic Acids in Aqueous Solution at Different Temperatures. GEORGE F. WHITE and HARRY C. JONES (*Amer. Chem. J.*, 1910, 44, 159—199).—In a preliminary paper (this vol., ii, 13), an account was given of the conductivity of several organic acids at temperatures between 0° and 35°. The work has now been extended to many other acids, and complete data are given for the conductivity and dissociation of all the acids examined. The conclusions arrived at previously are confirmed.

It is not possible to make any general statement with regard to the change in dissociation of the organic acids with change of temperature. With many of the acids, namely, acetic, propionic, phenylacetic, hippuric, malonic, maleic, fumaric, crotonic, benzoic, *m*-toluic, cinnamic, salicylic, and *m*-hydroxybenzoic acids, a maximum dissociation occurs between 25° and 35°. With other acids, namely, succinic, itaconic, racemic, methylsuccinic, citric, *p*-hydroxybenzoic, gallic, aniline-*m*- and -*p*-sulphonic, and *o*- and *p*-aminobenzoic acids, the dissociation increases from 0° to 35° without a maximum, but several of these give indications that a maximum would appear at a slightly higher temperature. The dissociation of *n*- and *iso*-butyric, mandelic, citraconic, mesaconic, *o*-toluic, and *o*-phthalic acids decreases regularly with rise of temperature from 0°. It is therefore obvious that isomeric acids do not behave similarly with respect to change in dissociation. The migration velocities of isomeric ions are identical. The dissociation of the organic acids in relation to temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants, and, since maxima in dissociation occur with many of the acids, it is evident that some other force or forces must be exerted in such cases.

E. G.

Electrical Resistance of the Alkali Metals. L. HACKSPILL (*Compt. rend.*, 1910, 151, 305—308).—The specific resistances of sodium, potassium, rubidium, and cæsium at different temperatures are recorded, and the results, except in the case of sodium, shown to be considerably lower than those obtained by Guntz and Broniewski (Abstr., 1909, ii, 113). The determinations were made in tubes completely filled with the metal in order to avoid the presence of the inert gases employed by Guntz and Broniewski.

W. O. W.

Simple Relation between the Size of the Atoms of Metals and the Temperature-coefficient of the Resistance. FRANZ STREINTZ (*Ann. Physik*, 1910, [iv], 33, 436—440).—It is shown that for certain series of metals the cube-root of the atomic volume is proportional to the temperature-coefficient of the electrical resistance between 18° and 100°. Palladium, platinum, aluminium, silver, gold, cadmium, and tin form such a series, and the data for zinc, lithium,

and mercury indicate that the proportionality factor has approximately the same value as for the metals of this series. The proportionality factor is, however, to some extent dependent on the atomic volume of the metal, being greater for metals of atomic volume less than 8·9 and smaller when the atomic volume exceeds 16·3. This variation is considered with reference to the data for lead, bismuth, thallium, sodium, potassium, copper, iron, nickel, glucinum, and cæsium. H. M. D.

Hydration and Molecular Heat of Ions in Very Dilute Aqueous Solutions. GUSTAV MIE (*Ann. Physik*, 1910, [iv], 33, 381—399).—A theoretical paper in which the equilibrium between the undissociated molecules and the ions of an electrolyte is examined from a kinetic point of view. The free ions are supposed to undergo hydration in stages, and this process requires a certain time which is comparable with the average period during which the ions exist as such in the aqueous solution before re-combination takes place. Since the average life of the ions diminishes as the concentration of the electrolyte increases, it follows that the ions are less hydrated in concentrated than in dilute solutions. In very dilute solutions the average hydration of the ions reaches a constant maximum value, and it is shown that for such solutions the rate of re-combination of the ions can be calculated by means of Langevin's formula.

The free energy of the ionisation process and the coefficient of ionisation are shown to be dependent on the degree of hydration, and these relationships are considered with reference to experimental data for solutions of potassium chloride and acetic acid. H. M. D.

Chemical Actions and Ionisation. G. REBOUL (*Compt. rend.*, 1910, 151, 311—312. Compare Abstr., 1909, ii, 718; Broglie and Brizard, Abstr., 1909, ii, 535, 637).—The author has repeated the experiments on the oxidation of sodium and the interaction of ammonia and hydrogen chloride, recently called into question by Broglie and Brizard (this vol., ii, 11), and maintains the accuracy of his observations. When nitric oxide and oxygen are allowed to combine in the apparatus already described, no electrical charge is developed if the apparatus is constructed of platinum, whereas when it is made of copper or brass, a charge is produced, probably through the action of the gas on the electrodes. W. O. W.

Electro-capillary Phenomena with Fused Salts. G. VON HEVESY and RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1910, 74, 443—465).—The arrangement of the apparatus, which was used for temperatures up to 800°, corresponded with that of the ordinary capillary electrometer; the electrodes were of graphite, and the glass capillary was about 1 mm. in diameter and 10 cms. long.

The system made up of fused lead in contact with fused lead chloride showed no electro-capillary phenomena. The following systems, however, gave results closely resembling those obtained with the ordinary mercury–sulphuric acid electrometer: Pb | KCl; Pb | KI,KCl; Pb | NaI,NaCl; Sn | LiCl,KCl; Hg | $LiNO_3,KNO_3$. The curves were of parabolic form in each case, but the relative extent of the

rising and falling branches varied considerably. The position of the maxima of the curves when lead was used with different electrolytes only varied between 1·36 and 1·44 volts, although the temperatures differed by as much as 200°.

The sensitiveness of these electrometers is only about 1/1000 that of the ordinary capillary electrometer. The following systems: Hg | BaI_2 in pyridine, and Hg | KCl in fused antimony trichloride, are of the same order of sensitiveness as those made up with fused salts.

The effect of the addition of lead chloride to fused potassium chloride in the system Hg | KCl has been measured, and from the results the equilibrium concentration of lead chloride in the system $Pb + 2KCl \rightleftharpoons PbCl_2 + 2K$ has been calculated.

The above results are shown to be qualitatively in complete accord with the accepted theory of electro-capillary phenomena

G. S.

Arc Characteristics in Gases and Vapours. MASAMICHI KIMURA and KIYOSHI YAMAMOTO (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 47—58).—The connexion between the voltage, current, and the length of arc which could be maintained between a carbon cathode and a water-cooled copper anode surrounded by various gases and vapours has been determined. The gases and vapours used were hydrogen, hydrogen mixed with benzene, methyl alcohol, a mixture of methyl alcohol and ethyl alcohol (composition not stated), ethyl alcohol, and air. For a given current and a given length of arc, the arc in an atmosphere of hydrogen, or of hydrogen mixed with benzene vapour, requires a larger voltage than in the case of the other vapours and of air. The gases and vapours mentioned above are arranged in the order of their relative efficiency for the production of undamped electrical oscillations. T. S. P.

Compressibilities of Helium and Neon. FRANK P. BURT (*Trans. Faraday Soc.*, 1910, 6, 19—25).—The apparatus described by Gray and Burt (Trans., 1910, 95, 1659) has been used to obtain the pressure-volume isothermals of helium and neon at 0°.

In the case of helium, pv is constant from 838 mm. to 147 mm. pressure. With neon the value of pv varies from 58·944 at 860 mm. to 58·886 at 144 mm. A tendency in the values at low pressures to be abnormally high with both gases is attributed to a constant error in the apparatus.

A straight line isothermal could be drawn between the twenty-one values of pv for neon obtained by smoothing the experimental values. The compressibility coefficient of neon between 0 and 1 atm. pressure is +0·00105, that is, neon, like hydrogen, is an ultraperfect gas. The compressibility coefficient of helium between the limits of pressure studied is zero. Helium behaves like a gas with a much higher critical temperature than it really possesses. R. J. C.

Compressibility Coefficients of Liquids. W. A. SUCHODSKI (*Zeitsch. physikal. Chem.*, 1910, 74, 257—276).—A modified form of

the Oersted-Röntgen compressibility apparatus, so designed that it can conveniently be kept at any desired constant temperature, is described. With this apparatus the compressibilities, β, at comparatively low pressures of a number of pure liquids at temperatures in the neighbourhood of 14°, 35°, and (in some cases) 100° have been determined. The values of $\beta \times 10^6$, corrected for the compression of the glass, are as follows: Ethyl bromide, 113·4 at 13·7°, 138·4 at 35°; ethyl ether, 163·0 at 12·2°, 206·9 at 34·8°; amylene, 170·5 at 16·7°, 209·2 at 34·7°; benzene, 86·8 at 12·9°, 100·3 at 34·9°, and 189·8 at 99·9°; fluorobenzene, 87·7 at 13·9°, 102·6 at 35·3°, and 189·8 at 99·7°; chlorobenzene, 67·1 at 13·3°, 77·0 at 35·4°, and 127·4 at 100·4°.

The formula $\beta = 0{\cdot}0006 V/T$, in which the symbols have the usual significance and apply for the boiling point in each case, is deducted by means of certain approximations from van der Waals' equation, and admits of the calculation of β at the boiling point of the liquid in question, both from density determinations and from the volume measurements of Kopp. It is shown that the observed and calculated values of β for non-associated liquids are in fair agreement. G. S.

Thermal Expansion of Metals. EDUARD GRÜNEISEN (*Ann. Physik*, 1910, [iv], **33**, 33—64. Compare Abstr., 1908, ii, 563).—The dependence of the thermal expansion of various metals on the temperature has been examined. The data of previous observers were made use of in the case of platinum, palladium, copper, silver, aluminium, iron, nickel, and iridium. For magnesium, zinc, cadmium, antimony, iridium, gold, lead, and bismuth, new measurements of the linear expansion between −183° and +100° have been made. It is found that the observed expansion is, in general, in close agreement with that required by Thiesen's exponential formula, $l_2 - l_1 = \gamma(T_2^{1+\epsilon} - T_1^{1+\epsilon})$, and this agreement is particularly good at low temperatures. Zinc, cadmium, and tin are, however, exceptions, and the abnormal behaviour in these cases is supposed to be due to discontinuous changes in the structure of the metals.

The experimental data do not indicate whether the above formula can be employed for extrapolation to temperatures in the neighbourhood of absolute zero. They show, however, that the exponent ϵ is a periodic function of the atomic weight of the metal, and that its maximum values are reached when the atomic volumes are at their respective minima. H. M. D.

Influence of Temperature and Pressure on the Coefficient of Expansion and the Specific Heat of Metals. EDUARD GRÜNEISEN (*Ann. Physik*, 1910, [iv], **33**, 65—78. Compare previous abstract).—From a comparison of the mean coefficients of expansion and the mean specific heats of the metals enumerated in the previous paper for the two temperature intervals −190° to 17° and 17° to 100°, the author finds that the influence of temperature is the same in the two cases, Within the limits of experimental error the ratio of the expansion coefficient to the specific heat is independent of the temperature. It follows from this that the variation of the specific heat with the temperature can be represented by Thiesen's exponential formula.

From measurements of the compressibility of aluminium, iron, copper, silver, and platinum at different temperatures, it is found that the relative changes of the density and of the specific heat, which are brought about by a given change of pressure, are of the same order of magnitude. H. M. D.

Use of Cooling Curves in Determining the Cryoscopic Point of Solution. M. MOULIN (*J. Chim. Phys.*, 1910, 8, 321—330). —When a dilute solution, losing heat energy at a constant rate by cooling, becomes supercooled, the separation of a particle of solid causes an abrupt rise in temperature to the freezing point. Since, however, a certain amount of solid is deposited in this process, the temperature observed is rather lower than the true freezing point of the original solution. The cooling curve presents a rapid fall during the liquid phase, a sudden rise to a maximum from the supersolubility point, followed by a gradual fall during separation of the solid. When the last part of the curve is extrapolated to cut the first part, the true freezing point is found. The experimental maximum is not sharply defined, owing to lag in the thermometer readings, but this lag does not affect the accuracy of the freezing-point values.

Cooling-curve determinations of molecular weight have been made with carbamide, sugar, and resorcinol in water, naphthalene in benzene, and water in acetic acid. R. J. C.

Impossibility of Superheating a Solid. A. BERTHOUD (*J. Chim. Phys.*, 1910, 8, 337—339).—It is possible to supercool a clear liquid because the very minute crystal nuclei which tend to form possess a surface energy greater than massive crystals and redissolve. If a drop of the liquid phase is placed on a solid at its melting point, it wets the surface and tends to spread as far as possible over it. Hence the solid has its surface energy diminished by contact with its liquid, and is thereby predisposed to melt rather than become superheated. Superheating would only be possible with a solid which on melting gave a liquid which did not wet its surface.

Sodium chloride hydrate, $NaCl,2H_2O$, which usually decomposes at $-12°$, was heated to $+15°$ by Frankenheim (1861), but this is a case of arrested decomposition, as the true melting point of the hydrate is probably $+15°$ or above. R. J. C.

Freezing-point Curves of Gaseous Mixtures: Compounds of Methyl Ether and Methyl Alcohol with Ammonia. GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1910, 151, 528—530. Compare Abstr., 1909, ii, 545).—The freezing-point curve for the system methyl alcohol-ammonia shows a well-defined maximum corresponding with the compound $MeOH,NH_3$. The curve for mixtures having 80—95% of alcohol could not be investigated, owing to the existence of uncrystallisable glasses. The curve for methyl ether–ammonia has a maximum corresponding with the formula OMe_2,NH_3, but this is not well defined owing to dissociation. W. O. W.

Application of Thermal Analysis to Several Binary Organic Systems. DEMETRIUS E. TSAKALOTOS and PHILIPPE A. GUYE (*J. Chim. Phys.*, 1910, **8**, 340—357. Compare Wroczynski and Guye, this vol., ii, 699).—The liquidus curves of the following mixtures are normal, and show no sign of additive compounds: phenol + benzene, benzene + thiophen, nitrobenzene + ethyl ether, aniline + chloroform. Benzene and thiophen form no eutectic, the freezing-point curve being characteristic of isomorphous mixtures. Freezing-point determinations were not possible with mixtures of phenol and benzoyl chloride, owing to the production of hydrogen chloride even at low temperatures. For a similar reason mixtures of bromine with benzene could not be studied.

Trichloroacetic acid with ethyl ether and acetone with chloroform give mixtures so viscous that freezing-point determinations are impracticable. The system acetone + chloroform in the presence of potassium hydroxide gives an additive product melting at 97°, namely, $CMe_2\cdot OH,CCl_3$. On mixing the components without alkali an appreciable amount of heat is liberated. This evidence and also the high viscosity point to the formation of an additive compound (compare Tsakalotos, Abstr., 1908, ii, 260).

The high viscosity of ethyl ether with trichloroacetic acid is held to indicate the formation of an additive compound in which the ether functions as a basic substance. The mixture with 69% of acid sets to an isotropic mass at −60°. Mixtures of aniline and ethyl acetate behave in a similar way (this vol., ii, 699),

The authors have determined the freezing-point of purified ethyl ether to be −112·1°, a value in agreement with that given by Ladenburg and Krügel (−112·6°), but not with that of Olszewski (−117·4°) or Guttmann (−117·6°). R. J. C.

Cryoscopy of the Naphthylamines and their Additive Compounds. ABEL BUGUET (*Compt. rend.*, 1910, **151**, 312—313).—The freezing-point curve for mixtures of chloro-2 : 4-dinitrobenzene shows two minima and a single maximum, the latter corresponding with the existence of the *hydrochloride* of 2 : 4-dinitrophenyl-α-naphthylamine. This has also been obtained in large, garnet-red crystals, m. p. 69°, by mixing the constituents in anhydrous solvents. The *hydrochloride* of 2 : 4-dinitrophenyl-β-naphthylamine has m. p. 65°. Mixtures of these salts with naphthalene give freezing-point curves having minima at 51·5° and 73° respectively. *m*-Dinitrobenzene gives W-shaped curves with α- and β-naphthylamine, and in each case garnet-red crystals of additive compounds were isolated, having m. p. 60—63° and 57° respectively. W. O. W.

Thermodynamic Calculation of the Vapour Pressure of Water and Ice. WALTHER NERNST (*Ber. Deut. physikal. Ges.*, 1910, **12**, 565—571).—The value recently obtained by Scheel and Heuse (*Ann. Physik*, 1910, [iv], **31**, 715) for the vapour pressure of water at 50° has been employed to recalculate the constants in the thermodynamic equation for the vapour pressure of water. The vapour-pressure values calculated from the new equation are in almost complete agreement with the measured values for temperatures

between 0° and 50°; considerably greater differences are found between 50° and 100°.

The recent determinations of the specific heat of ice between $-10°$ and $-200°$ are also utilised in the determination of the constants involved in the thermodynamic equation for the vapour pressure of ice. Calculated and observed pressures are shown to be in satisfactory agreement. H. M. D.

Relations between the Properties of Liquids at the Boiling Point. DAN TYRER (*Phil. Mag.*, 1910, [vi], 20, 522—533).—An empirical relationship connecting the latent heat of vaporisation and the molecular volume of a liquid at its boiling point has been found to hold for a large number of organic compounds. This is expressed by $L.M = K\sqrt[3]{V}$, in which L is the latent heat, M the molecular weight, V the molecular volume, and K a constant. By taking $K = 1583$, it is shown that the calculated heats of vaporisation are in good agreement with those found by experiment. The only classes of substances which do not seem to conform to this relationship are the aliphatic hydrocarbons and ethers, and also associated liquids. For associated liquids which do not dissociate on vaporisation the calculated latent heats are greater than the observed values. On the other hand, for associated liquids which dissociate on vaporisation, the calculated heat values are greater or smaller than those found by experiment according to the magnitude of the heat of dissociation.

By combining the above relationship with Trouton's rule, the molecular volume and the boiling temperature are shown to be connected by the equation $T = K_1\sqrt[3]{V}$. For the various members of a homologous series, an approximately constant value of K_1 is obtained, but this value varies appreciably from one series to another. For aliphatic hydrocarbons and ethers, $K_1 = 68$; for aliphatic chlorides and amines, $K_1 = 70$; for aliphatic esters and bromides, $K_1 = 74$; for aliphatic iodides and aromatic hydrocarbons, $K_1 = 79$, and for aromatic ethers, $K_1 = 83$. The relationship is also affected by molecular association, the value of K_1 being much greater for associated than for normal liquids. H. M. D.

Determination of Boiling Point. I. Fall of Temperature in Vapours of High Molecular Complexity at Small Pressures. CHRISTIAN J. HANSEN (*Zeitsch. physikal. Chem.*, 1910, 74, 65—114. Compare Abstr., 1909, ii, 212, 969).—An apparatus suitable for the investigation of the distillation of compounds of high boiling point under the pressure of their own vapour is figured and described in detail. The liquid to be distilled was heated electrically when necessary, and the distillation vessel provided with a jacketing arrangement, by means of which it could be heated from the outside to any desired temperature. One of the main objects of the investigation was to measure the variation of temperature along the column of vapour. This was at first effected by thermometers placed at different levels in the tube, and in the final form of apparatus by a thermocouple which could be moved up and down in the vapour.

Experiments were made with palmitic, stearic, myristic, and lauric

acids under the most varying conditions, and the results are described in detail. Under certain conditions it makes comparatively little difference whether the distillation flask is jacketed or not. The experiments with the thermocouple show clearly that the temperature gradually rises as the couple is progressively raised in the column of vapour. The effect of different degrees of internal heating is fully discussed. It was found that there is a great tendency for the solutions to become superheated. Some experiments were made with palmitic acid without internal heating, and in these experiments the difference in temperature between the upper and lower thermometers was remarkably constant, amounting to about 0·4° per cm.

A method proposed by von Rechenberg, according to which the distilling flask is completely immersed in a bath, did not lead to satisfactory results. G. S.

Heat of Formation of the Oxides of Cobalt and Nickel and the Heat of Combination of Acidic Oxides with Sodium Oxide. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1910, [iv], **30**, 193—201. Compare this vol., ii, 585).—The quantities of heat liberated in the oxidation of cobalt, nickel, zinc, and manganese, and certain of the lower oxides of these metals, have been measured. From the experimental data the following thermal values are derived: $Co + O = CoO$ (crystalline) $+57·5$ cal.; $Co + O = CoO$ (amorphous) $+50·5$ cal.; $3Co + 4O = Co_3O_4 + 193·4$ cal.; $Co + 2O + Na_2O = Na_2CoO_3 + 100·2$ cal.; $Zn + O + Na_2O = Na_2ZnO_2 + 87·0$ cal.; $Mn + 3O + Na_2O = Na_2MnO_4 + 169·0$ cal., and $MnO_2 + O + Na_2O = Na_2MnO_4 + 49·4$ cal. The oxidation of nickel by means of sodium peroxide is very incomplete, and the thermal data are considered to be somewhat untrustworthy. The actual results seem to show, however, that the heat of formation of the oxide is practically the same as in the case of cobalt: $Ni + O = NiO + 57·9$ cal. H. M. D.

Heat of Combustion of Some Hydronaphthalene Derivatives. HENRI LEROUX (*Compt. rend.*, 1910, **151**, 384—387).—The following results have been obtained for the heats of combustion of liquid naphthalene and its products of hydrogenation: naphthalene, -19 Cal. (solid, $-14·6$ Cal.); dihydronaphthalene, -25 Cal.; tetrahydronaphthalene, 4 Cal.; hexahydronaphthalene, 6 Cal.; octahydronaphthalene, 33 Cal., and naphthane, 61 Cal. These values are in accordance with the facts already known in connexion with the hydrogenation of naphthalene, and in the author's opinion are best explained by Bamberger's formula for this hydrocarbon.

W. O. W.

Heat of Hydration. III. WILLEM P. JORISSEN (*Chem. Weekblad*, 1910, **7**, 761—768. Compare this vol., ii, 269).—An application of the author's method of determining heat of hydration to zinc sulphate, manganese sulphate, magnesium sulphate, sodium phosphate, sodium carbonate, and strontium chloride, and a comparison of the values obtained with those given by Thomsen A. J. W.

Variations of the Physical Properties of Metallic Alloys Subjected to Mechanical and Thermal Action. I. Specific Gravity. E. PANNAIN (*Gazzetta*, 1910, **40**, i, 431—433).—The experiments were carried out with coinage bronze (about 4% tin) and silver (16·5% copper), and they show that a marked increase in specific gravity is produced by hammering, the increase being maintained or, rather, increased after a subsequent annealing. Bronze of D 8·76965 after being annealed and hammered (alternately) three times, and coined, had D 8·94623. Coinage silver of D 9·99932 had D 10·21636 after a similar treatment. R. V. S.

The Rectilinear Diameter for Oxygen. ÉMILE MATHIAS and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, **151**, 474—475. Compare this vol., ii, 771).—This paper contains the summarised numerical results of the determinations outlined in a previous communication. It is shown that the diametral line for oxygen is very nearly rectilinear. The densities of liquid oxygen at low temperatures are not in agreement with those of Dewar (1893) or of Baly and Donnan (Trans., 1902, **81**, 911). W. O. W.

Nature of the Transition Layer between Two Adjacent Phases. WILLIAM C. McC. LEWIS (*Phil. Mag.*, 1910, [vi], **20**, 502—511).—The values obtained for the internal pressure of a liquid differ considerably according to whether these are calculated from van der Waals' equation or from the work required to remove unit volume from the surface layer of the liquid outside the range of molecular attraction. This divergence is supposed to be due to the average density in the surface layer being greater than the ordinary bulk density.

From Bakker's equation for the latent heat of vaporisation, the relationship $\lambda_i = a/v_s$ is deduced, in which λ_i is the internal heat of vaporisation, a the van der Waals' constant, and v_s the average volume of one gram of the substance in the surface layer. From this relationship the average surface densities of sixteen liquids are calculated for their respective boiling points. The values thus obtained are approximately 2·5 times the bulk densities of the liquids.

In the case of water, the surface density has been calculated for temperatures between 0° and 100°. As the temperature rises the densities converge somewhat, the ratio falling from 2·189 at 3·6° to 2·023 at 100°. The temperature variations of the internal pressure, both in the bulk and in the surface layer, are also tabulated.

The change in the density of water, which is involved in its transition from the bulk of the liquid to the surface layer, is accompanied by a heat effect which is calculated to be 0·0034 cal. per unit area of surface. This is of the same order as the heat effect found by Parks on moistening powders with water. H. M. D.

Variation with Temperature of Viscosities of Gases of the Argon Group. A. O. RANKINE (*Proc. Roy. Soc.*, 1910, *A*, **84**, 181—192. Compare this vol., ii, 409).—In comparing gaseous

viscosities at 100° with those at room temperature, a correction $(1-2\gamma\theta)$ is necessary, where γ is the coefficient of linear expansion of the glass capillary tube, and θ the temperature interval. The correction due to alteration of the mean free path of the molecules is negligible, but a small unknown error is introduced by the alteration in surface tension of the mercury pellet which constitutes the driving piston.

The viscosity of air and the argon gases increases by about 20—25% when the temperature is raised to 100°. Assuming that the increase follows a linear law, $\eta_\theta = \eta_0(1+\beta\theta)$, where η_θ is the viscosity at temperature θ, the values of the temperature-coefficient, $\beta \times 10^5$, are: air, 266; helium, 232; neon, 221; argon, 283; krypton, 308; xenon, 339. The actual viscosities at 0°, $\eta_0 \times 10^4$, are: air, 1·879; neon, 2·981; argon, 2·102; krypton, 2·334; xenon, 2·107. The temperature-coefficients of viscosity are not proportional to the viscosities.

According to Sutherland the temperature-coefficient of gaseous viscosity is $\sqrt{T}(1+C/T)$, where T is the absolute temperature and C a constant depending on the attraction between the molecules of the gas. The values of C calculated by the author are: air, 116; helium, 70; neon, 56; argon, 142; krypton, 188; xenon, 252. Certain of these are in fair accord with values obtained by Rayleigh and by Schultze. A simple ratio, about 1·14, exists between C and the critical temperature in the case of argon, krypton, xenon, nitrogen, oxygen, carbon dioxide, ethylene, and nitrous oxide. With helium and hydrogen, the value of C is much higher than this relation indicates, although for a perfect gas C should be zero.

The mutual attraction between the molecules, C, which has the effect of making collisions more frequent may be expressed in terms of an increase in cross sectional area of the molecule, $1:(1+C/T)$. The author calculates the molecular volume and molecular density of the argon group relative to helium. The size and density of the atoms apparently increase with increase in atomic weight. R. J. C.

The Internal Friction of Albumin Solutions. W. PAULI and R. WAGNER (*Biochem. Zeitsch.*, 1910, 27, 296—303).—The internal friction of serum albumin solutions in the presence of varying quantities of hydrochloric acid was determined, and found to attain a maximum when the latter was $0·02n$ and when the concentration of the protein was 1·7%. This shows a deviation for the number obtained by Michaelis and Mostynski (this vol., ii, 592). The authors criticise the investigations of Michaelis on the determination of the isoelectric point of proteins, and maintain that the solutions employed were not sufficiently pure, that the globulins had been separated by half-saturation with ammonium sulphate, and that the solution containing the albumin had not been dialysed for a sufficient length of time, and contained a certain amount of combined ammonia, showing therefore the isoelectric point in the presence of a higher concentration of acid. S. B. S.

Anomalous Adsorption. WILHELM BILTZ and HANS STEINER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 113—122).—It is found that

the adsorption of night-blue by cotton wool increases at first with the concentration of the solution and then decreases in more highly concentrated solutions of the colouring matter. This behaviour is not in accordance with the exponential adsorption formula, and is regarded as an example of anomalous adsorption. The relationships are essentially the same whether technical or dialysed night-blue is used in the experiments; they are qualitatively the same whether the absorption takes place at the ordinary temperature or in boiling solutions. Similar effects have also been observed in the adsorption of night-blue by animal charcoal and of victoria-blue and Congo-red by cotton wool, and it is pointed out that like deviations from the exponential formula have also been found in the adsorption of copper sulphate by clay and of agglutinin by bacteria.

In the case of night-blue, victoria-blue, and copper sulphate, the observed effects are supposed to be due to hydrolysis of the substance in solution, the hydrolysed base being adsorbed. The relatively large amount of adsorption in dilute solution is attributed to the increased hydrolysis, and the effect of temperature in reducing the degree of abnormality is shown to be consistent with this hypothesis. Observations relating to the adsorption of benzopurpurine, alizarincyanine green-G extra, and acid-alizarin-blue are also recorded which show that in these cases the adsorption is more or less normal.

H. M. D.

Thermal Dissociation of Calcium Carbonate. JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1910, **32**, 938—946).—The work of previous authors on the equilibrium pressure of the reaction $CaCO_3 \rightleftarrows CaO + CO_2$ has been rendered somewhat inaccurate by a lack of definiteness in the temperature of the reacting system. In the present investigation this error has been obviated by using a very small quantity (0·1 gram) of material, so that the extreme variation throughout the charge did not exceed 2°. The apparatus employed and the mode of determining the temperature are described.

The results of four series of measurements are expressed by the equation $\log p = (-9340/T) + 1{\cdot}1 \log T - 0{\cdot}0012T + 8{\cdot}882$, where p is the equilibrium pressure in mm. of mercury at the absolute temperature T. This equation represents the results much better than Riesenfeld's formula (this vol., ii, 126). E. G.

Thermodynamics of the Capillary Layer of a Pure Substance between the Homogeneous Liquid and Vapour Phases. GERRIT BAKKER (*Zeitsch. physikal. Chem.*, 1910, **73**, 641—666. Compare Abstr., 1907, ii, 434).—A mathematical paper. Equations are deduced which give the relationships between the different factors determining the nature of the capillary layer separating the vapour and liquid phases of a pure substance for different degrees of curvature of that layer. An expression is deduced for the internal heat of evaporation, and it is shown that when the capillary layer becomes flat (that is, of infinite radius) the expression reduces to the well-known Clapeyron-Clausius equation. Another equation gives the mean thickness of a cylindrical capillary layer in terms of the curvature,

surface tension, and other factors concerned, and it is shown that when the radius of the layer is infinite, liquid and vapour contribute to the capillary layer in quantities proportional to their densities. When the law of Cailletet and Mathias (law of the rectilinear diameter) holds, the mean thickness of a flat capillary layer is a diminishing linear function of the temperature. G. S.

Surface Tensions of Some Unsaturated Organic Compounds. FREDERICK H. GETMAN (*Amer. Chem. J.*, 1910, **44**, 145—158).—On account of the value of surface-tension measurements for the determination of molecular complexity, the author is carrying out a systematic investigation of the surface tension of a series of closely related unsaturated organic compounds. The present paper deals with mesityl oxide, β-dimethylacrylic acid, styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin. The measurements were made by the capillary method, the apparatus employed being a modification of that used by Przyluska (this vol., i, 106).

The results are arranged in tables, which record the observed capillary elevation, the density, the surface tension, and the coefficients of variation of molecular surface tension at various temperatures. Curves have been constructed in which the surface tensions are plotted as ordinates and the temperatures as abscissæ. All the substances examined, except dimethylacrylic acid, have been found to be non-associated. The values of n (the number of atoms in the molecule) obtained by this method agree closely with those calculated by means of Longinescu's formulæ (Abstr., 1903, ii, 531) correlating the number of atoms in the molecule of a substance with the absolute boiling or melting point and the density. The average values of the coefficient k in Ramsay and Shields' formula for the non-associated compounds are in all cases greater than 2·12, the mean value assigned by Ramsay and Shields. The association of β-dimethylacrylic acid decreases slowly with increase of temperature. E. G.

Studies of the Processes Operative in Solutions. XI. The Displacement of Salts from Solution by Various Precipitants. HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1910, *A*, **84**, 123—136. Compare Abstr., 1907, ii, 848).—Previous measurements of the precipitating influence of ethyl alcohol and hydrogen chloride on various salts have been repeated, and the study has been extended to methyl and propyl alcohols, dextrose, etc. The new determinations made at 25° and 0° reveal small errors in the previous work, but do not affect the general conclusions.

Particular care was taken to obtain pure salts, which were centrifugalised to remove occluded mother liquors, and graded to obtain particles of uniform size and remove fine powder. Slight differences in solubility between different samples of the same salt render it necessary to compare each solubility in presence of a precipitant with the original solubility of the same sample of salt.

As before, the effect of precipitants is calculated as if it were a simple dehydrating one and expressed as "apparent molecular hydration" of the precipitant. The value obtained denotes the amount

of water thrown out of action as solvent water without postulating any particular mechanism by which the precipitant acts.

The action of the non-electrolytes, methyl alcohol, ethyl alcohol, and propyl alcohol, is exactly comparable with that of hydrogen chloride, although less intense. Of the three alcohols, methyl is the least and propyl the most active precipitant. Of the chlorides, ammonium chloride is least and potassium chloride most affected. Sodium chloride occupies an intermediate position, and exhibits the peculiarity that at 0° small amounts of precipitant produce less effect than at 25°. In all other cases the precipitants are more active at 0° than at 25°. Although the superior effect produced by hydrogen chloride must be attributed to a direct dehydrating action, the precipitants do not act merely by attracting water. Methyl alcohol, which is the more soluble and presumably more hydrated, is not so active a precipitant as propyl alcohol. The effect of the precipitant is to increase the proportion of hydrone (H_2O) and the other simpler molecules present in water, which in virtue of their tendency to polymerise and form water condition the dehydration of the hydrolated solute molecules. The greater effectiveness of the precipitant at 0° may be due to the greater complexity of the water, giving more opportunity for the precipitant to depolymerise it; also to the larger proportion of complex, easily precipitated, salt molecules.

The reduction of molecular conductivity of the salts by the three alcohols is exactly parallel to the reduction in solubility. In all cases the effect is greater at 0° than at 25°. Increased solubility is noticed with potassium chloride in presence of potassium nitrate and potassium and sodium chlorides in presence of dextrose. In the latter case a compound of salt with sugar is held responsible, whereas in the former it is supposed that the nitrate has a depolymerising effect on the chloride. Potassium chloride acts as a precipitant of the nitrate. In general, the nitrates are more easily precipitated than chlorides, in accordance with the view that nitrates have less affinity for water than chlorides.

The precipitation of salts from solution is mainly due to dehydration changes, conditioned not only by the direct removal of water from the solution by the precipitant, but also, in the case of neutral precipitants particularly, by the agency of the increased proportion of hydrone molecules produced in the water by the mechanical interposition of the molecules of the precipitant. R. J. C.

Is the Iron-Nickel Meteorite Stable or Metastable? W. GUERTLER (*Zeitsch. physikal. Chem.*, 1910, 74, 428—442).—Fraenkel and Tammann (Abstr., 1909, ii, 157) have brought forward evidence to show that meteoric iron-nickel is unstable, but the author attempts to show from the available data that this is not the case. The different structure of the meteoric alloy is ascribed to the action of a force tending to draw similar constituents together, corresponding with the tendency of small crystals in contact with a saturated solution to pass into larger crystals. It is shown that the formation of the characteristic meteoric structure can occur only at low temperatures, and as the "collective crystallisation" process is extremely slow under such con-

ditions, it can only be fairly complete when unlimited time is available, as in the case of a meteorite. G. S.

Transformation of Amorphous into Crystalline Substances. Cornelio Doelter (*Zeitsch. Chem. Ind. Kolloide,* 1910, **7**, 86—92. Compare this vol., ii, 696).—In reference to the view that the "amorphous" and crystalline forms of a substance are not essentially different, the author discusses the influence of the size of the particles on the physical properties. Experiments are described which show that slightly soluble mineral substances, which have been precipitated in "amorphous" form, can be readily converted into a definite crystalline form by shaking with water for considerable periods of time. The same effect is produced without shaking if the amorphous substances are heated in contact with water at 60—70°. H. M. D.

Crystallisation from Aqueous Solutions. IV. Robert Marc (*Zeitsch. physikal. Chem.,* 1910, **73**, 685—723. Compare Abstr., 1908, ii, 160; 1909, ii, 798, 983).—Many of the experiments described in the previous papers have been repeated by more accurate methods, and the majority of the earlier results are confirmed. The conductivity method of following the results has proved to be inaccurate, more particularly in the early stages of the reaction, and in the present series of experiments the concentrations have mostly been determined by direct analysis.

The reaction is of the second order only up to 13°; above that temperature the speed of crystallisation is simply proportional to the supersaturation of the solution.

Further evidence is adduced that the retarding effect of dyes is connected with adsorption. It is shown that the dyes retard crystallisation proportionally to the extent to which they are adsorbed, and, further, they act by diminishing the active mass in the surface layer. In the presence of dyes, the solutions approach an apparent point of equilibrium with the same velocity constant as they approach the true equilibrium point in the absence of dyes.

The results are not sufficiently accurate to admit of the establishment of a relationship between concentration and amount adsorbed. The rate of crystallisation in the presence of dyes is also of the first order at relatively high temperatures. G. S.

Classification of Disperse Systems. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide,* 1910, **7**, 155—157).—A modification of Ostwald's classification of the various types of colloidal solutions is suggested. H. M. D.

Examples of Compound Disperse Systems. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide,* 1910, **7**, 157—158).—When concentrated solutions of the thiocyanates of the alkaline earth metals are mixed with a concentrated solution of manganese sulphate, the alkaline earth sulphates are precipitated in a colloidal (gelatinous) form having a cellular structure. If the containing vessels are rapidly cooled in liquid air, the intercellular solution solidifies to a

clear glass, and the systems thus obtained are regarded as examples of compound disperse systems. H. M. D.

Theory of the Production and the Stability of Colloidal Solutions. I. P. P. von Weimarn (*Koll. Chem. Beihefte*, 1910, 1, 396—422).—A theoretical paper in which the author discusses the so-called dispersion and condensation methods for the production of colloidal solutions. Condensation methods are regarded as dependent on the retardation of crystallisation processes, and dispersion methods on the retardation of processes of solution. H. M. D.

Coexistence of the Crystalline and Colloidal States. H. Schade (*Koll. Chem. Beihefte*, 1910, 1, 391—395).—Microscopic observations show that the formation of crystals of cholesterol from an alcoholic solution is preceded by a separation of the substance in the form of liquid drops. Similar effects are found in the case of solutions in ethyl ether and in oils, and also when the pure molten substance is rapidly cooled. The freshly-formed, needle-shaped crystals are very plastic, but this plasticity diminishes with time. The plastic condition is supposed to be associated with the presence of a portion of the cholesterin in the colloidal state, the colloidal form being gradually transformed into the crystalline modification. H. M. D.

Moulding of Gels by Crystals. Raphael E. Liesegang (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 96—98).—Observations are recorded which show that the crystallisation of substances from jellies, in consequence of the removal of water, frequently leads to the formation of characteristic gelatin aggregations. H. M. D.

Formation of Concretions in the Process of the Separation of Emulsion Colloids. H. Schade (*Koll. Chem. Beihefte*, 1910, 1, 375—390).—The author discusses the part played by colloids in the formation of the special structures which are found in gall-stones, pearls, and hail-stones. H. M. D.

Influence of the Degree of Dispersion on the Stability of Chemical Compounds and the Decomposition of the Elements. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 93—96). —A theoretical paper in which the author examines the influence of the degree of dispersion of a dissolved or volatile substance on the equilibrium between the liquid or vapour containing the disperse substance and the corresponding solid phase. Conditions under which compounds and elements must dissociate as a consequence of the character of the disperse phase are indicated. H. M. D.

Alkali Hydroxides. I. The Binary Systems: Sodium and Potassium Hydroxides; Potassium and Rubidium Hydroxides, and Sodium and Rubidium Hydroxides. Georg von Hevesy (*Zeitsch. physikal. Chem.*, 1910, 73, 667—684).—The complete equilibrium curves of the three binary systems in question have been determined. The substances were heated in a silver vessel in an

atmosphere of nitrogen, and the temperature measurements were made with a silver-nickel thermocouple, which is very suitable for working between -80° and 920°. All four alkali hydroxides have a transition point at temperatures below the respective melting points, and the positions of these transition points in the binary systems have also been determined and are represented graphically.

The melting points and transition points of the pure substances are as follows: sodium hydroxide, $318{\cdot}4 \pm 0{\cdot}2^\circ$, $299{\cdot}6 \pm 0{\cdot}5^\circ$; potassium hydroxide, $360{\cdot}4 \pm 0{\cdot}7^\circ$, $248 \pm 0{\cdot}5^\circ$; rubidium hydroxide, $301 \pm 0{\cdot}9^\circ$, $245 \pm 0{\cdot}5^\circ$; cæsium hydroxide, $272{\cdot}3 \pm 0{\cdot}3^\circ$, $223 \pm 0{\cdot}5^\circ$. Rubidium hydroxide has D^{11} 3·203; for caesium hydroxide, D^{11} 3·675.

Sodium and potassium hydroxides are completely miscible both in the liquid and solid states; the freezing-point curve has a minimum at 187° and 38·7 atom per cent. of potassium hydroxide. The transition curve is of the same form as the freezing-point curve.

Potassium and rubidium hydroxides are also completely miscible both in the liquid and solid states, but the freezing-point curve shows two maxima at 399° and 87 atom per cent. and 351° and 22·3 atom per cent. of potassium hydroxide, as well as a minimum at 306° and 65·6 atom per cent. of potassium hydroxide. The transition diagram is of similar form. There is no definite evidence as to whether the maxima correspond with definite compounds of the two hydroxides.

Sodium hydroxide and rubidium hydroxide are not miscible between 80·8 and 37·6 atom per cent. of the latter compound. There is a maximum on the curve at 278° and 30·7 atom per cent. of rubidium hydroxide, which may correspond with the formation of a compound, $(NaOH)_2,RbOH$, although the evidence is not conclusive. There is no maximum on the transition diagram of this system.

From the thermal data, the latent heat of fusion and the heat of transition have been calculated by methods given by Tammann (compare Abstr., 1905, ii, 229; this vol., ii, 17). The latent heats of fusion per mol. are 1602, 1606, 1614, and 1609 cal., and the heats of transition per mol. are 990, 1522, 1702, and 1763 cal. for sodium, potassium, rubidium, and cæsium hydroxides respectively. G. S.

The Equilibrium of the Reciprocal Salt Pairs: $KCl + NaNO_3 \rightleftarrows KNO_3 + NaCl$. Kenjiro Uyeda (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, **2**, 245—261).—The following measurements have been made, the temperature being 25°: (1) The composition of the saturated solution when both sodium and potassium chloride are present as solid phases. One hundred grams of water contain 29·88 grams of sodium chloride and 16·28 grams of potassium chloride (compare Soch, Abstr., 1899, ii, 84). (2) The solubility in solutions of varying concentrations of potassium chloride in sodium chloride, and vice versa. (3) The composition of the saturated solution when both potassium chloride and nitrate are present as solid phases. One hundred grams of water contain 34·62 grams of potassium chloride and 22·88 grams of potassium nitrate (compare Soch, *loc. cit.*). (4) The solubility in solutions of varying concentrations of potassium nitrate in potassium chloride, and vice versa. (5) The composition of the saturated solution when both potassium and sodium nitrates are present as solid phases. One

hundred grams of water contain 100·10 grams of sodium nitrate and 46·35 grams of potassium nitrate. (6) The solubility in solutions of varying concentrations of sodium nitrate in potassium nitrate, and vice versa. (7) The composition of the saturated solution when both sodium nitrate and chloride are present as solid phases. One hundred grams of water contain 23·74 grams of sodium chloride and 56·56 grams of sodium nitrate (compare Soch, *loc. cit.*). (8) The solubility in solutions of varying concentrations of sodium chloride in sodium nitrate, and vice versa. (9) The composition of the saturated solution when sodium chloride, sodium nitrate, and potassium nitrate are together present as solid phases. One hundred grams of water contain 23·59 grams of sodium chloride, 63·26 grams of sodium nitrate, and 42·55 grams of potassium nitrate. (10) The solubilities in solutions of varying concentrations of sodium nitrate and potassium nitrate together in sodium chloride, of sodium chloride and sodium nitrate together in potassium nitrate, and of sodium chloride and potassium nitrate together in sodium nitrate. (11) The solubilities in solutions of varying concentrations of sodium chloride and potassium chloride together in potassium nitrate, and of potassium nitrate and potassium chloride together in sodium chloride.

The results are expressed graphically in various diagrams.

T. S. P.

Equilibrium Solid–Liquid–Gas in Binary Systems which Present Mixed Crystals. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 206—210).—The equilibrium between *p*-dichloro- and *p*-dibromo-benzene when mixed crystals, liquid, and vapour are present has been investigated. Data are recorded which show the dependence of the initial melting point and the initial solidifying point on the composition of the mixed crystals, and, further, the pressure and composition of the vapour which is in equilibrium with mixed crystals of varying composition and the corresponding liquid phase.

In the estimation of the composition of the saturated vapour, a measured volume of this was passed through a heated tube containing calcium oxide; the calcium chloride and bromide thus obtained were determined by adding a known excess of silver nitrate to the nitric acid solution, weighing the precipitate obtained, and estimating the excess of silver by Volhard's method.

H. M. D.

Equilibrium in the Ternary System: Water, Potassium Carbonate, Potassium Ethyl Dipropylmalonate. J. W. M'DAVID (*Proc. Roy. Soc. Edin.*, 1910, **30**, 440—447).—When a concentrated aqueous solution of potassium ethyl dipropylmalonate is shaken with a concentrated aqueous solution of potassium carbonate, two distinct layers are formed (compare Crichton, Trans., 1906, **89**, 929). The peculiarity of this case lies in the fact that both substances are salts of the same metal.

The composition of the two layers has been determined for different concentrations of the three components. The percentage of potassium ethyl dipropylmalonate was determined by precipitating a weighed quantity of the solution with dilute sulphuric acid, and titrating the

hydrogen ethyl dipropylmalonate with baryta. The potassium carbonate was determined by titration with acid, using phenolphthalein as indicator.

In order to produce equilibrium when a mixture is diluted, some potassium carbonate passes from the lower to the upper layer. In concentrated solutions there is a considerable quantity of potassium carbonate in the upper layer, whereas the amount of potassium ethyl dipropylmalonate in the potassium carbonate (lower) layer is very small, and it is only when the solutions are comparatively dilute that there is any appreciable increase in the amount of ester salt in the lower layer. At 25° the two layers become identical when the solution contains 11·6% of potassium ethyl dipropylmalonate, 20·6% of potassium carbonate, and 67·8% of water.

The effect of temperature on the equilibrium was determined, experiments being carried out at 2°, 25°, and 56°. When the mixture is such that the upper layer contains about 48% of potassium ethyl dipropylmalonate, the effect of temperature is very small. The critical solution at 25° becomes opalescent at 25·4°, but there is no apparent change on cooling to zero.

The temperature at which the two solid phases and the two liquid phases are present at the some time is probably in the vicinity of 46°; it could not be determined exactly, owing to the extreme viscosity of the liquid. Owing to the same cause, the solubility of the pure potassium ethyl salt could not be determined.

Solutions of sodium ethyl dipropylmalonate have the same properties with regard to a solution of sodium or potassium carbonate as the potassium ethyl salt has to either of these solutions. T. S. P.

Conditions for the Precipitation of Uric Acid and its Salts from Solutions. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1910, 67, 332—403. Compare His and Paul, Abstr., 1900, i, 591; Gudzent, *ibid.*, 1909, i, 434, 435; Little, *ibid.*, 1909, ii, 331).—The system water, phosphoric acid, sodium hydroxide, and uric acid has been examined; the concentration of the phosphoric acid was kept constant, so that the system could be regarded as one of three components, and the results represented graphically in a triangle. Phosphoric acid was never found in the solid phase.

A series of solubility determinations were made with the phosphoric acid of given concentration (2·076 grams of phosphoric oxide per litre) as solvent. All experiments show that uric acid readily tends to form supersaturated solutions, but after some time, or in the presence of air, the supersaturation disappears, and it may be due to the presence of metastable lactamurates (Gudzent).

Attempts made to determine the concentration of the solution in equilibrium with uric acid and monosodium urate in the presence of the given amount of phosphoric acid showed that the same solution is not obtained when uric acid is shaken with a solution of dihydrogen phosphate as is formed when uric acid is shaken with the disodium phosphate. The equilibrium solution was calculated, however, with the aid of Gudzent's and His and Paul's determinations. The value found was, for 100,000 molecules, 34·2 mols. Na_2O, 1·76 mols. uric

acid, and 26·3 mols. P_2O_5. The solubility curves of uric acid and of monosodium urate are given.

The results are given in the form of diagrams, and the meaning of these is discussed. It is pointed out that the solid phase which is deposited, its amount, and the concentration of uric acid in the final solution are all given by means of the diagram.

Similar experiments have been made with the potassium compounds. The equilibrium solution contains 38·67 mols. K_2O, 3·20 uric acid, and 26·3 P_2O_5.

The results give some idea of the behaviour of uric acid in urine, but in this case the phenomena are more complex, owing to the presence of neutral salts, for example, sodium chloride, and of colloids.

The sedimentum lateritium, which consists mainly of quadurate, is metastable in the system sodium (potassium) oxide, phosphoric acid, uric acid, water. In urine it is rather more stable.

The quadurate is formed frequently when uric acid is precipitated, owing to rapid cooling.

Solubility determinations in the system sodium oxide, uric acid, and water have been made, and the solubility curve of monosodium urate determined. Even in the presence of strongly alkaline liquids the disodium urate is never met with as the solid phase. J. J. S.

Velocity of the Reaction between Colloidal Sulphur and Silver Sulphate. M. RAFFO and A. PIERONI (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 158—160).—Colloidal sulphur, obtained by the action of sulphuric acid on sodium thiosulphate, reacts with a solution of silver sulphate according to the equation : $3Ag_2SO_4 + 4H_2O + 4S = 4H_2SO_4 + 3Ag_2S$. In dilute solution the precipitate first formed has a yellow colour, but this quickly changes to red, and finally to black. Measurements of the rate at which the silver sulphate is reduced show that the reaction proceeds according to the equation for a unimolecular change. From this it is evident that the reaction takes place in stages, and the differently coloured precipitates are supposed to represent the intermediate products.

Colloidal sulphur reacts with a solution of stannous chloride on warming, with the evolution of hydrogen sulphide and the precipitation of stannous sulphide. It liberates iodine from a solution of iodic acid, and yields hydrogen sulphide quite readily with nascent hydrogen. These experiments show that colloidal sulphur is much more reactive than other forms of sulphur. H. M. D.

Velocity of Saccharification of Starch. I. HENRI VAN LAER (*Bull. Acad. roy. Belg.*, 1910, 611—641).—Brown and Glendinning have shown (Trans., 1902, **81**, 388) that the hydrolysis of starch by diastase does not take place in accordance with the logarithmic law, whilst V. Henri (*Lois générales de l'action des diastases*, Paris, 1903) takes the view that it does, and suggests that the discrepancy in results may be due to differences in (1) method of determining the limiting value of the hydrolysis; (2) temperature, or (3) the ferment used. The present investigation has been undertaken to determine the origin of the discrepancy, and in this part the hydrolysis of starch by dilute

acids is dealt with, and it is shown that this follows the same law as the hydrolysis of sucrose by dilute acids, whatever may be the physical condition of the starch employed.

Special precautions were taken to guard against initial alkalinity of the starch used. It was observed that an opalescent starch solution (2%), prepared under a pressure of 4 atmospheres, showed no reducing power, passed easily through filter paper, was retained completely by parchment paper, gave a filtrate containing 0·375% of starch when filtered through collodion membrane, underwent no apparent change even under a pressure of 2 atmospheres at atmospheric temperature when mixed with hydrochloric acid, but became less opalescent and in time as limpid as water (although it still gave a blue colour with iodine) when mixed with diastase.

The results of the quantitative experiments made, which are tabulated in detail in the original, showed that (1) k varied very little with the time; (2) hydrolysis proceeded in the same manner whether starch mucilage, "soluble starch," or "soluble starch filtered through a collodion membrane" was the initial product used; (3) the rate of hydrolysis remained proportional to the concentration of starch when this did not exceed 5·5%, but fell off for higher concentrations; (4) the hydrolytic power of different acids for starch was proportional to their hydrolytic power for sucrose or their electric conductivity; (5) the rate of hydrolysis by sulphuric acid always increased with the concentration of the acid, but more slowly than this for dilute starch solutions, and more rapidly than this for concentrated starch solutions. T. A. H.

Specific Stereochemical Behaviour of Catalysts. LEOPOLD ROSENTHALER (*Zeitsch. physikal. Chem.*, 1909, **73**, 760—761).—Fajans (this vol., ii, 599) has suggested that the "asymmetric synthesis" of *d*-benzaldehydecyanohydrin discovered by the author is really due to an asymmetric decomposition of the symmetrical nitrile assumed as the primary product of the reaction, but it is now shown that this suggestion is untenable. G. S.

The Relative Principle and the Representation of Physical Phenomena in Space of Four Dimensions. PHILIPP FRANK (*Zeitsch. physikal. Chem.*, 1910, **74**, 466—495).—A theoretical paper in which a method of representing phenomena in space of four dimensions is described, and the advantages illustrated by application to optical phenomena in moving bodies and to certain electrodynamic phenomena. G. S.

Shape of the Molecule. RICHARD D. KLEEMAN (*Phil. Mag.*, 1910, [vi], **20**, 445—450).—If σ_1 is the radius of the sphere of action of a molecule of a liquid, the molecular volume of which is V, then at corresponding temperatures the ratio V/σ_1^3 should be the same for all liquids if the molecules are spherical in shape.

An examination of a number of different organic compounds from this point of view indicates that the molecules are not spherical. The relationships involved are, however, consistent with the assumption that the molecules consist of oblate spheroids. H. M. D.

Gas Washing Bottles with Very Slight Resistance to the Passage of a Gas. ALEXANDER CHARLES CUMMING (*Trans. Faraday Soc.*, 1910, 6, 10—13).—Three modified forms of gas washing apparatus are described which are designed to produce the maximum washing effect with the minimum back pressure. In all of these the gas passes through a by-pass arranged near the surface of the washing liquid, and by its passage causes the liquid to circulate, so that the by-pass is continuously refilled from the main reservoir. R. J. C.

Inorganic Chemistry.

The Constitution of Water (*Trans. Faraday Soc.*, 1910, 6, 71—123).—The following five papers formed the basis of a general discussion on the constitution of water.

Constitution of Water. Is Water an Electrolyte? PAUL WALDEN (*Trans. Faraday Soc.*, 1910, 6, 71—78).—According to the Thomson-Nernst rule, liquids with a dielectric constant as high as water ($D = 80$) should have great dissociating power on dissolved water, and enable it to function as an electrolyte. Water dissolved in liquid hydrogen cyanide ($D = 95$) has a very small or zero conductivity, whereas the conductivities of binary salts in the same solvent are very high. The conductivity of water dissolved in formamide ($D > 84$) is very small, and practically does not increase with dilution. In formic acid ($D = 58{\cdot}5$) the conductivity of water is at least ten times as great, although the ionising power of the solvent is less. Nitrosodimethylamine ($D = 53{\cdot}3$), although of less viscosity than formic acid, gives water solutions of less conducting power.

The conductivity of water dissolved in sulphuric acid ($D > 84$) is of a much higher order than any of the above, but the conductivities of all the substances mentioned dissolved in water are parallel to the conductivities when water is the solute.

The physical theory failing to account for the above facts, a chemical hypothesis is necessary. The author suggests that water becomes a good electrolyte when its solvent is distinctly acidic or basic. The amphoteric water must previously form with the solvent a kind of salt. The same chemical forces act when water is the ionising solvent.

R. J. C.

The Chemical Nature of Molecular Association: a Special Study of the Case of Water PHILLIPE A. GUYE (*Trans. Faraday Soc.*, 1910, 6, 78—85).—Estimates of the degree of polymerisation of liquids based on the surface-tension values are subject to an unknown error, due to the difference in composition between the surface layer and the main bulk of the liquid.

Dutoit and Mojoiu's formula connecting molecular weight with

surface tension gives a lower association factor than that of Ramsay and Shields, and leads to the conclusion that water at 0° is mainly trihydrol, and at the boiling point dihydrol. Since polymerisable substances are the more associated the greater the number of centres of association they contain, dihydrol should polymerise more readily than monohydrol. The formation of highly complex stable polyhydrols may accompany the phenomena of colloidal hydrates. The equilibrium of hydrol (H_2O) and dihydrol (H_4O_2) in the liquid phase is subject to the equation $C_2 = KC_1^2$, where C_1 and C_2 are the concentrations of hydrol and dihydrol respectively. In the gaseous phase $C_2^1 = K^1(C_1^1)^2$. Assuming that K^1 has the same value as K, it may be calculated that the association factor of the liquid phase $x = [2v(1+y) - y^2 - y\sqrt{\{4v(1+y)+y^2\}}] \div \{v(1+y) - 2y^2\}$, where y is the ratio of concentration of hydrol to dihydrol in the gaseous phase, and v the volume of vapour formed from unit volume of liquid at the same temperature. From the published values of y and v, the author calculates that the association factor of liquid water is 1·90 at 80°, 1·86 at 100°, and 1·82 at 120°, values very close to those obtained by Dutoit and Mojoiu.

According to the above equation, the polymerisation of only 1% of the vapour molecules corresponds with an association factor 1·58 in the liquid phase. As little as 1 in 10,000 polymerised gaseous molecules corresponds with an appreciable polymerisation of the liquid. Pressure has but little influence on the degree of association, but since the pressure in the surface film is greater than in the bulk of the liquid, the polymerisation in the surface layer will be higher, as indicated by the values calculated by Ramsay and Shields.

R. J. C.

Liquid Water a Ternary Mixture: Solution Volumes in Aqueous Solutions. William R. Bousfield and Thomas M. Lowry (*Trans. Faraday Soc.*, 1910, **6**, 85—104. Compare Abstr., 1905, ii, 135).—It has been shown that the abnormal contraction in water between 0° and 4° is eliminated when 2% or more of dissolved sodium hydroxide is present, and also that the solution volumes of moderately concentrated sodium hydroxide attain a maximum value at about 70°.

Solution volumes represent the actual volume occupied by the solute minus the contraction which takes place during dissolution, and are more symptomatic of changes in the solvent (depolymerisation and association with solute) than in the solute. The simpler character of the solution-volume curves of concentrated solutions suggests that changes in hydration are of less importance than changes in the molecular weight of the solvent, and that the observed diminution in solution volumes at the higher temperatures takes place in spite of progressive dehydration which would lead to an increase in volume. The authors have already suggested that not only is dissolved ice present in liquid water at low temperatures, but dissolved steam molecules at temperatures approaching the boiling point. The same suggestion was made by Callendar (*Phil. Trans.*, 1902, *A*, **199**, 147) in discussing the specific heat and thermal expansion of water, and the

compressibility values strengthen this view. The density of combined water is calculated to be 1·1 in the case of potassium chloride associated with about 10 molecular proportions of water. This is taken as the density of dihydrol, ice (H_6O_3) and steam (H_2O) occupying greater bulk.

Measurements have been made of solution volumes of chloral hydrate, sucrose, acetic acid, silver nitrate, and potassium, sodium, lithium, and calcium chlorides. The salts all show a maximum in the solution-volume curve, which is the more pronounced the lower the concentration, that is, the greater the relative disturbance of the condition of the solvent. The solutes, acetic acid, chloral hydrate, and sucrose, with small affinity for water exhibit no maxima, but the solution-volume curves have a distinct tendency to droop. Passing to the more hydrated solutes, the maximum occurs at lower and lower temperatures until with lithium chloride it is at 35°. This appears to be almost the limit possible, since any further lowering would be rendered difficult by the increasing proportions of ice molecules in the solvent.

R. J. C.

Constitution of Water. WILLIAM SUTHERLAND (*Trans. Faraday Soc.*, 1910, 6, 105—116. Compare Abstr., 1906, ii, 603).—The author maintains his view that liquid water is a mixture of dihydrol and trihydrol. A geometrical structure representing a trihydrol molecule, the atomic diameter of oxygen and hydrogen being derived from the gas constants, gives 1·2 as the density as compared with 0·917, the actual density of ice. If the molecule were spinning in every plane it would sweep out a sphere, and its density would work out at a much lower figure than 0·917, so that a molecule of ice must be relatively fixed and its energy internal.

Since ionisation, when possible, is supposed to be complete, the proportion of hydrol in water (completely ionised) must be very small, the proportion of H^+ and OH^- ions being known to be very small. Highly polymerised chains of hydrol molecules probably occur in colloidal hydrosols and hydrogels, each end of the chain being electrically attached to an amphoteric nucleus which the author terms a "semplar."

The density of water of crystallisation in thirty-one salts examined by Clarke is practically constant, 18 grams occupying 13·76 c.c. In $LiSO_4,H_2O$ the volume of water (13·3 c.c.) is very near the mean. It is argued that water of crystallisation is always in the same form as in lithium sulphate, that is, solid hydrol of density 1·31. Liquid hydrol would have density about 1·26, that is, higher than dihydrol. Water of crystallisation has a dielectric capacity of the same order as sodium chloride, whereas that of liquid water is twelve times as great. The molecular refraction of water of crystallisation is about 4·22, whereas in liquid water and ice the value is about 6·0. The specific heat of water of crystallisation, of ice and steam at constant pressure are each about 0·5, so that liquid water is abnormally high.

In melted crystals the water has specific heat about 1·0, indicating that a profound change occurs in water of crystallisation on melting.

R. J. C.

The Specific Heat of Ice, Water, and Water Vapour. WALTHER NERNST (*Trans. Faraday Soc.*, 1910, **6**, 117—119. Compare this vol., ii, 263).—The molecular heat-temperature curves of ice, water, and steam are mapped from the most recent data. The water and ice curves are enterpolated to absolute zero (molecular heat $=0$).

In the case of steam, assuming that the molecules possess energy of rotation in three planes at right angles, the molecular heat cannot be less than $8R/2=7{\cdot}94$, and this value is practically reached at room temperature. The molecular heat is, therefore, supposed to remain constant, and the curve is a straight line from 350° abs. to absolute zero.

The course of the molecular heat curves is in agreement with the hypothesis of a polymerisation : $2H_2O=(H_2O)_2+2519$ cal. By means of the data given it is possible to calculate the vapour-pressure curves of ice and water down to very low temperatures. R. J. C.

Ultra-microscopy of Iodine Solutions. II. J. AMANN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 67—70. Compare this vol., ii, 496).—Further observations are recorded relating to the appearance of iodine solutions when examined by the ultra-microscope, and to the changes which are brought about by the action of light. The solvents used were chloral, molten chloral hydrate, phosphorus chloride, phosphoryl chloride, iodine trichloride, amyl acetate, pyridine, nitrobenzene, acetaldehyde, chloral alcoholate, propylamine, sulphuric acid, and peppermint oil. On the basis of the colour of the solutions and the ultra-microscopic observations, the solvents examined in this and the previous paper are divided into six groups, and these are then subdivided, so that in all seventeen different types of iodine solutions can be distinguished. H. M. D.

Some Analogies between Derivatives of Oxygen and Nitrogen. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 29—36).—Attention is drawn to the analogy, displayed in many of their reactions, between hydrogen peroxide, hydroxylamine, and hydrazine. R. V. S.

Exact Atomic Weights of Oxygen and Silver. GUSTAV D. HINRICHS (*Compt. rend.*, 1910, **151**, 513—515. Compare Abstr., 1907, ii, 945; Dubreuil, Abstr., 1909, ii, 653, 654).—In a previous paper (Abstr., 1909, ii, 653) the author has described a method for calculating the analytical excess ($=\epsilon$), or difference between the experimental and absolute values of the atomic weights. A table is now given containing a résumé of the values of ϵ calculated from 656 determinations of the atomic weights of oxygen and silver made between 1810—1910. The conclusion is drawn that the true atomic weights of these elements are 16 and 108 respectively, since in 70% of the determinations ϵ is negligibly small. W. O. W.

Solubility of Oxygen in Molten Silver. FREDERICK G. DONNAN and T. W. A. SHAW (*J. Soc. Chem. Ind.*, 1910, **29**, 987—990).—The

solubility of oxygen in fused silver was determined by measuring the contraction occurring when silver is fused in an atmosphere of oxygen. Ten grams of melted silver at 1020° and under a pressure of 751 mm. absorb 20·5 c.c. of oxygen (measured at 0° and 760 mm.), a result which is practically identical with that obtained by Sieverts and Hagenacker (Abstr., 1909, ii, 1004). From the results of Sieverts and Hagenacker it is calculated that the freezing point of silver saturated with air (only the oxygen is absorbed) should be lowered by 10·4°; the experimental number is 7°. T. S. P.

Complexity of Tellurium. WILLIAM R. FLINT (*Amer. J. Sci.*, 1910, [iv], **30**, 209—219. Compare Browning and Flint, Abstr., 1909, ii, 996).—Five hundred grams of purified tellurium were oxidised by nitric acid and converted into the tetrachloride by repeated evaporation with hydrochloric acid. The solution was diluted with a large volume of boiling water, and the precipitated dioxide dissolved in slight excess of hydrochloric acid and reprecipitated by further addition of a large volume of water. After a series of ten fractionations by this hydrolytic method, 23 grams of dioxide were obtained. By the basic nitrate method, the atomic weight of the metal in this sample of dioxide was found to be 124·32, whereas the same method, applied to the original material, gave 127·45. The author considers that the complexity of tellurium, purified by the usual methods, has been definitely established by these results, and the value 124·3 represents the nearest approach which has yet been made to the true atomic weight of tellurium. In support of the view that fractional hydrolysis of the chloride leads to a gradual separation, it is found that the product obtained after four fractionations gave an atomic weight 126·59, and after eight fractionations 125·37.

Preliminary experiments relating to the less readily hydrolysed fraction are also described. The tellurium in the filtrates from the above hydrolytic processes was recovered by treatment with ammonia and acid, the dioxide dissolved in hydrochloric acid, and the solution diluted with a large volume of boiling water. The filtrate from the precipitated dioxide was then heated to boiling, ammonia and acetic acid added, and the less easily hydrolysed fraction thus obtained was subjected to three further operations of the same kind. By this series of fractionations a sample of dioxide weighing about 10 grams was obtained. On fractionating this by addition of successive quantities of ammonia to the boiling hydrochloric acid solution, 8 grams of an orange-coloured, crystalline substance, 2 grams of a yellow, crystalline substance, and 0·1 gram of a pale green, substance were obtained. These substances were tested for iron, copper, bismuth, and antimony with negative results. In hydrochloric acid solution all three give black precipitates with stannous chloride similar to that obtained with ordinary tellurium. On addition of excess of ammonia to the solution of the green substance, the precipitate obtained is not completely dissolved by the excess of alkali. Both the soluble and insoluble portions, when dissolved in hydrochloric acid, give a black precipitate with stannous chloride. These results indicate that tungsten is not present. H. M. D.

Relations between White Phosphorus, Red Phosphorus, and Pyromorphic Phosphorus. PIERRE JOLIBOIS (*Compt. rend.*, 1910, **151**, 382—384. Compare Cohen and Olie, Abstr., 1909, ii, 998).—The author denies the validity of Cohen and Olie's conclusion that red phosphorus is not an individual modification. This view is not in agreement with the observations already published (Abstr., 1909, ii, 726) or with new experiments described in the present communication.

The vapour pressure at different temperatures has been determined for red and white phosphorus, and for the new pyromorphic form (*loc. cit.*). The results are plotted in logarithmic curves, from which the conclusion is drawn that the latter is stable below 450°, the ordinary red modification between 450—610°, whilst white phosphorus is in equilibrium above 610° (compare Chapman, Trans., 1899, **75**, 734). The same results were obtained in direct determinations of the transition points. Hittorf's phosphorus, obtained by crystallisation from lead, appears to be a mixture of ordinary crystallised phosphorus with the pyromorphic variety. The abnormally high density is due to the presence of lead. W. O. W.

The Hydrates of Disodium Hydrogen Phosphate. ICHITARO KITAWAKI (*Mem. Coll. Sci. Eng. Kyōtō*, 1909—1910, **2**, 237—239).—Shiomi (Abstr., 1909, ii, 573) has observed three breaks in the solubility curve of disodium hydrogen phosphate, namely, at 36·45°, 48·0°, and 95·2°. The break at 36·45° corresponds with the transition from dodecahydrate to heptahydrate, and it is now found that the two other breaks correspond with the transitions from heptahydrate to dihydrate, and from dihydrate to anhydrous salt respectively.

The *dihydrate* was isolated by fusing the dodecahydrate in its water of crystallisation and evaporating the resulting solution at a temperature of 70—75°. The anhydrous salt was obtained from a similar experiment carried out in the neighbourhood of 99·5°.

T. S. P.

The Boiling Point of Sodium Chloride. FRIEDRICH EMICH (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1910, ii, 65).—Using Burgess' method (Abstr., 1908, ii, 41), the boiling point of sodium chloride was found to be 1750°. T. S. P.

Action of Sodium Carbonate on Insoluble Carbonates. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 512—515).—The experiments were made on the same lines as with solutions of the alkali nitrates (see following abstract), boiling aqueous solutions of sodium carbonate being used. Barium and strontium carbonates are not attacked. Cadmium carbonate is only affected by strong solutions of sodium carbonate, some cadmium oxide being formed. Dolomite and magnesium, lead, and zinc carbonates are all attacked. With calcium carbonate (washed chalk) concordant results could not be obtained.

Calcium phosphate is attacked by boiling solutions of either sodium or potassium carbonate. T. A. H.

Action of Lithium Nitrate on Insoluble Carbonates. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 332—334).—In previous papers the results of investigations on the action of sodium or potassium nitrate on carbonates insoluble in water have been given (this vol., ii, 411, 612). On applying the same methods with boiling aqueous solutions of lithium nitrate, it was found that barium, calcium, magnesium, zinc, and lead carbonates were all attacked, whilst strontium and cadmium carbonates were not affected. It was necessary to use dilute solutions in the case of barium and very dilute solutions in the case of magnesium in order to detect these metals in presence of lithium. T. A. H.

Bolognian Stones. II. LUDWIG VANINO and EMILIE ZUMBUSCH (*J. pr. Chem.*, 1910, [ii], 82, 193—204. Compare Abstr., 1909, ii, 731).—It has been shown previously that the quantity of sulphur employed in the preparation of Bolognian stones affects their luminescence. The quality of the sulphur is, however, immaterial, since at a high temperature all varieties of sulphur are changed into the same modification. The quality of the lime is of prime importance. Ordinary builder's lime and Kahlbaum's "calcium oxide *pro analysi*" are useless; ignited limestone forms good stones, but the best results are obtained with Kahlbaum's lime prepared from marble. The three last-mentioned limes are shown to be alike chemically, to exhibit the same flame spectrum, and in solution to have practically the same alkalinity and electrical conductivity. The difference in their efficiency must be attributed, therefore, to their difference in physical structure, on account of which the limes have different velocities of reaction. This explanation can be tested experimentally, since it is well known that calcium oxide prepared from the nitrate is remarkably inactive towards chemical reagents, whilst the oxide prepared from the carbonate or the hydroxide is easily attacked, and also since it has been shown (*loc. cit.*) that the phosphorescence of Bolognian stones is mainly due to the presence of polysulphides; thus it is found that stones manufactured from calcium oxide prepared from the nitrate are of poor quality, and contain very little polysulphide, whilst similar stones made from the oxide prepared from the hydroxide or carbonate phosphoresce extensively, and exhibit a strong polysulphide reaction. So also stones prepared from Kahlbaum's oxide, from marble, or from ignited limestone give immediately a white turbidity when treated with sodium carbonate and then acidified, whilst the inefficient stones prepared from oxide "*pro analysi*" give only a feeble polysulphide reaction many seconds after acidification.

The oxides of barium and of strontium, which are too fusible to be used alone in the preparation of Bolognian stones, have a very beneficial effect when employed in conjunction with the carbonates. Good stones are obtained from a mixture of strontium carbonate (20 grams), sulphur (3 grams), lithium carbonate (0·5 gram), and thorium nitrate (1 c.c. of 0·5% alcoholic solution), or from a mixture of barium carbonate (20 grams), sulphur (3 grams), lithium carbonate (0·5 gram), and rubidium carbonate (0·3 gram), but the phosphorescence of stones produced when one-half of the strontium or of the barium carbonate is

replaced by the corresponding hydroxide is still more intense, and exhibits a very much slower rate of decay.

Attention has also been given to the effects produced by the addition of minerals, containing rare earths or radioactive substances, to the mixtures used in the preparation of Bolognian stones. The addition of pitchblende, cleveite, or monazite almost or entirely destroys the phosphorescence; from mixtures containing fergusonite, moderately good stones can be prepared, but their quality is very much inferior to that of stones prepared from mixtures containing the usual salts of bismuth, thallium, etc.

Stones exceeding any others previously made in the intensity and duration of their phosphorescence have been prepared by the ignition, for three-quarters of an hour in a Rössler furnace, of the following mixture: calcium oxide (10 grams), strontium carbonate (10 grams), barium carbonate (10 grams), magnesium oxide (10 grams), sulphur (6 grams), potassium sulphate (1 gram), sodium sulphate (1 gram), lithium carbonate (2 grams), starch (2 grams), bismuth nitrate (2 c.c. of 0·5% solution), and thallium sulphate (2 c.c. of 0·5% solution). The stones exhibit a pale blue phosphorescence, which decays very much more slowly than that of even the best violet stones. When the ignition is prolonged to two hours, the phosphorescence is very intense and greenish-yellow; after three hours' ignition, the stones are no longer luminous. The finest and most intense green phosphorescence hitherto obtained is exhibited by stones prepared by igniting the following mixture for three-quarters of an hour: calcium hydroxide (10 grams), strontium oxide (10 grams), sulphur (3 grams), potassium sulphate (0·5 gram), sodium sulphate (0·5 gram), lithium carbonate (1 gram), starch (1 gram), bismuth nitrate (1 c.c.), rubidium nitrate (1 c.c.). The persistence of the phosphorescence is such that it is possible to read in darkness by the light of these stones one hour after their preparation.

Unsuccessful attempts have been made to intensify the phosphorescence of Bolognian stones by rubbing them with fluorescent substances, by keeping them in fluorescent solutions or in an atmosphere of hydrogen, carbon dioxide, or oxygen, and by gently warming them with potassium chlorate, potassium perchlorate, or barium peroxide.

The prejudicial effect of heat on Bolognian stones is shown by heating them in a fusible alloy of tin and lead, in molten zinc, and in molten silver; the phosphorescence, which is violet at lower temperatures, becomes blue and then pale blue at higher temperatures, and finally is changed to green shortly before its disappearance. Calcium stones can be kept at 80—100° for eight to ten hours without injury.

The sulphides of all the metals of the alkaline earths exhibit phosphorescence; stones prepared from magnesium oxide or sulphide, however, do not phosphoresce unless some calcium compound is present. C. S.

Hydration and Constitution of Portland Cement. SENDER KEISERMAN (*Koll. Chem. Beihefte*, 1910, 1, 423—453).—A summary is given of the more important views which have been put forward in

reference to the constitution and the hydration of Portland cement, and a new method of investigating the nature of the constituents of the material is described. This is based on the specific absorptive capacity which particular constituents possess for certain colouring matters. As the result of the examination of a large number of colouring substances, the author recommends patent-blue for the detection of alumina, alcoholic anthrapurpurin for free lime, neutral methylene-blue for free amorphous silica, and an acetic acid solution of methylene-blue for combined silica. From observations made with these reagents on the hydrated cement, the following conclusions are drawn. The fine needle-shaped crystals consist of hydrated calcium monosilicate; these are coloured by anthrapurpurin, but not by patent-blue. The amorphous constituent of the cement consists also of calcium monosilicate containing a larger proportion of water. The large, hexagonal crystals are calcium hydroxide, and the small, hexagonal plates are hydrated tricalcium aluminate. Experiments with the unhardened material (klinker) indicate that this in all probability consists of a conglomerate of dicalcium silicate and tricalcium aluminate in the ratio: $4(2CaO,SiO_2) + 3CaO,Al_2O_3$.

H. M. D.

The Solubility of Alkali Sulphates in Alkaline Solutions, and of Calcium Sulphate in Solutions of Alkali Sulphate and Free Alkali. JOH. D'ANS and O. SCHREINER (*Zeitsch. anorg. Chem.*, 1910, **67**, 437—441. Compare this vol., ii, 125).—The isotherms at 25° have been determined for certain solutions of alkali sulphates containing an excess of alkali hydroxide. The solubility of sodium, potassium, and ammonium sulphates is progressively lowered by the addition of increasing quantities of the corresponding alkali. Basic salts are not formed.

Gypsum is the stable solid in contact with a saturated solution of sodium sulphate at 25°, but when sodium hydroxide is added, calcium hydroxide becomes the stable solid, the limit being at 1·41 mols. Na_2SO_4 and 1·48 mols. NaOH in 1000 grams of solution. In solutions of potassium sulphate, the corresponding limit is between syngenite and calcium hydroxide. The change in concentration produced by adding ammonia to the limiting solution ammonium syngenite–gypsum is also determined.

C. H. D.

The Reaction between Strontium Sulphate and Sodium Carbonate. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **68**, 69—72).—The ratio $[Na_2CO_3]/[Na_2SO_4]$ in contact with strontium sulphate is found to be 0·0676 at 25°. The dissociation of the two salts may be neglected, being the same for both. From the above ratio, $[SrCO_3]/[SrSO_4]$ is 0·26. Calculation from the known solubilities of strontium sulphate and carbonate gives 0·13, a result of the same order. Freshly precipitated and washed strontium sulphate gives the same result as when dried at 70° or heated to redness. C. H. D.

Barium Nitride and its Relation to Nitrogen in Presence of Iron. DAFFY WOLK (*Bull. So . chim.*, 1910, [iv], **7**, 830—832. Compare Maquenne, Abstr., 1892, 776, and Guntz and Mentrel, Abstr., 1903, ii, 546).—It is shown that barium nitride may be

prepared by the direct action of nitrogen on heated barium amalgam. The amalgam used was prepared by Guntz' process (Abstr., 1902, ii, 138). It was heated in an iron crucible, surrounded by a nickel shell, the whole being placed in a porcelain tube, which was then thoroughly dried by passing in pure dry nitrogen and evacuating the tube. The temperature of the tube was gradually raised to 800° in the course of three hours and then to 1000°, when the nitrogen was rapidly absorbed, forming barium nitride, Ba_3N_2, as a brown powder, which was unstable in moist air, furnishing barium hydroxide and ammonia. The product contained a trace of ferric nitride, and the proportion of the latter was materially increased by (1) more rapid heating; (2) heating the barium amalgam in contact with a fragment of sheet iron. In such a mixed product the ferric nitride dissociated towards the end of the reaction, unless the quantity of barium nitride present was relatively high.

T. A. H.

Colloidal Barium Sulphate. YOGORO KATO (*Mem. Coll. Sci. Eng. Kyōtō*, 1909—1910, 2, 187—215).—Colloidal barium sulphate (compare Feilmann, Abstr., 1909, ii, 482) was obtained by adding an alcoholic solution of sulphuric acid (obtained by diluting a molar aqueous solution with twice its volume of alcohol) to the equivalent quantity of a molar solution of barium acetate diluted with six times its volume of alcohol. The resulting precipitate and milky solution were evaporated to dryness under diminished pressure, keeping the temperature below 40°, giving a translucent, casein-like residue, which was readily and completely soluble in water to a fluorescent colloidal solution.

Barium sulphate is a positive colloid, and the solution shows the usual precipitation reactions towards anions. Cations of higher valency hinder the coagulation. Barium chloride and nitrate do not cause coagulation except in highly concentrated solutions; moreover, the presence of barium ions hinders the coagulation by potassium chloride. Highly dissociated electrolytes have generally the stronger coagulating effect, but sodium citrate has a much lower coagulating power than citric acid. Barium chloride and ferric sulphate, which are known to be much occluded by precipitated barium sulphate, have comparatively small coagulative power. Electrolytes which, owing to hydrolysis, contain colloids in solution have an abnormal coagulating power, which is strong when the colloid is negative and weak when it is positive.

The adsorption by the barium sulphate gel in solutions of potassium nitrate, potassium sulphate, and barium chloride was determined by measuring the specific conductivity of their solutions in which the gel was suspended. The adsorption was very small, but was found to be in fair agreement with the ordinary adsorption formula. Measurements of the electrical conductivity before and after coagulation showed that slight adsorption took place when the barium sulphate was coagulated by potassium sulphate.

T. S. P.

Double Chlorides and Iodides of Zinc. FRITZ EPHRAIM and SAMUEL MODEL (*Zeitsch. anorg. Chem.*, 1910, 67, 379—386. Compare Abstr., 1908, ii, 693).—Two *calcium zinc chlorides*, $CaZnCl_4,5\cdot5H_2O$

and $Ca_2ZnCl_6,6H_2O$, may be obtained by mixing the components in suitable proportions, and form very hygroscopic crystals. The corresponding *strontium*, $SrZnCl_4,4H_2O$, and *barium* salts, $BaZnCl_4,4H_2O$, are described, the latter being only obtained when a warm solution is evaporated.

In addition to Rammelsberg's salt, $KZnI_3$, a second *potassium zinc iodide*, $K_2ZnI_4,2H_2O$, may be obtained by evaporating the solution on the water-bath until crystallisation begins, and then allowing it to remain for several days over sulphuric acid. It forms rather hygroscopic, transparent crystals, melting above 100°. Two *sodium zinc iodides*, $Na_2ZnI_4,3H_2O$ and $NaZnI_3,2H_2O$, of which the first was described by Rammelsberg, may be obtained. A second *ammonium zinc iodide*, $NH_4ZnI_3,4{\cdot}5H_2O$, forms very hygroscopic, hexagonal tablets. The *calcium*, *strontium*, and *barium* salts, $CaZnI_4,8H_2O$, $SrZnI_4,9H_2O$, and $BaZnI_4,4H_2O$, are described. C. H. D.

Behaviour of Solid and Fused Copper towards Gases. ADOLF SIEVERTS and WILHELM KRUMBHAAR (*Zeitsch. physikal. Chem.*, 1910, **74**, 277—307. Compare Stahl, *Metallurgie*, 1907, **4**, 769).—At high temperatures (1200°) oxygen is taken up by fused copper with the formation of cuprous and cupric oxides, and is not given up when solidification takes place in an atmosphere free from oxygen because of the small dissociation pressure of the oxides. Nitrogen, carbon monoxide, and carbon dioxide are insoluble both in solid and fused copper.

Both solid and fused copper absorb hydrogen. At constant pressure the solubility of hydrogen in solid copper increases in a linear manner as the temperature rises; at the melting point there is a sudden increase in solubility, and beyond that point the solubility again increases linearly with the temperature as far as the measurements were carried (1500°). At 623°, 919°, and the melting point, 100 grams of solid copper absorbs 0·084, 0·287, and 0·41 milligram of hydrogen, and at 1123°, 1276°, and 1520°, 0·608, 0·862, and 1·350 milligrams of hydrogen respectively are absorbed by 100 grams of fused copper: in each case at 760 mm. pressure. At constant temperature the amount of hydrogen absorbed by fused copper is proportional to the square root of the pressure. As even at 650° hydrogen diffuses slowly out of a copper tube, it is assumed that copper and hydrogen form solid solutions.

Sulphur dioxide is insoluble in solid copper, but dissolves readily in fused copper, and in this case, also, the solubility increases as the temperature rises. At 1123°, 1276°, 1327°, and 1500°, 100 grams of copper dissolve 0·453, 0·627, 0·705, and 0·950 gram respectively of sulphur dioxide at 760 mm. pressure. It is remarkable that in this case also the solubility is proportional to the square-root of the pressure. In the case of hydrogen, it is usually assumed that the gas is present in the copper in the atomic condition, but a similar explanation is excluded for sulphur dioxide. G. S.

Conditions which Determine the Composition of Electro-deposited Alloys. II. Silver–Copper. SAMUEL FIELD (*Trans. Faraday Soc.*, 1910, **6**, 1—9. Compare this vol., ii, 38).—Copper and silver are electrodeposited together only within very

narrow ranges of concentration, temperature, etc. With sulphates and nitrates, solutions containing an enormous preponderance of copper yield practically pure silver. With cyanides, copper begins to be deposited when the amount of silver is reduced to about 0·4 gram per litre. By further reduction of the silver concentration, deposits containing any proportion of copper are obtainable. The deposition of copper along with silver is promoted, not only by large excess of copper, but by decrease in the proportion of free potassium cyanide, increased current density, and low temperature of deposition. The conditions favourable to the deposition of copper in presence of silver are analogous to those necessary for the deposition of zinc in presence of copper. The silver compound used in the above experiments was prepared by dissolving washed precipitated silver cyanide in a minimum of potassium cyanide. The copper compound had the composition CuCN,KCN. The deposits were always of a powdery character, usually on account of the high current density used.

R. J. C.

Ternary Alloys of Copper, Antimony, and Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 69—75. Compare this vol., ii, 779).—Owing to the existence of the compound Cu_3Sb, which melts without decomposition, the ternary system Cu–Bi–Sb is divided into two others, namely, Cu–Cu_3Sb–Bi and Cu_3Sb–Sb–Bi. From their experimental results given in the present paper, the authors have constructed the diagram of the binary system Cu_3Sb–Bi, which is necessary for the study of the ternary systems mentioned above. The compound Cu_3Sb and bismuth are only partly miscible in the liquid state, and they form neither compounds nor solid solutions. At 640° two layers are formed, one rich in Cu_3Sb (87%), and the other rich in bismuth (92%). The eutectic is nearly pure bismuth. In all the alloys there is an indication at 390—400° of the transformation of β-Cu_3Sb into α-Cu_3Sb. Alloys which solidify below 400° deposit only α-Cu_3Sb. In conclusion, the general form of the diagram of the ternary system Cu_3Sb–Sb–Bi is discussed.

R. V. S.

Preparation of a Cuprous Nitrate, $CuNO_3,2NH_3$. W. H. SLOAN (*J. Amer. Chem. Soc.*, 1910, **32**, 972—973).—The *salt*,

$$CuNO_3,2NH_3,$$

has been prepared by leaving a solution of cupric nitrate in liquid ammonia in contact with copper foil until it became colourless. On allowing the ammonia to distil gradually from the solution, the cuprous nitrate crystallised. It was not obtained quite pure, but contained a few blue crystals of cupric nitrate. The salt rapidly undergoes oxidation in the air.

E. G.

The Ammonia Compounds of Mercuric Bromide. RAGNAR WIDMAN (*Zeitsch. anorg. Chem.*, 1910, **68**, 1—25. Compare Gaudechon, Abstr., 1909, ii, 670; this vol., ii, 296).—The following compounds

can exist in contact with solutions containing mercuric bromide, ammonium bromide, and ammonia in different concentrations: $HgBr_2,2NH_3$; NH_2HgBr; $NH(HgBr)_2$; $Hg_9N_4Br_6$; and NHg_2Br, and probably no others.

The compound $HgBr_2,2NH_3$ is formed on adding an excess of ammonia to a solution of mercuric bromide and much ammonium bromide. The compound NH_2HgBr is obtained from it by loss of ammonium bromide, in contact with a solution containing little of this salt. When the bromide concentration falls still lower, NHg_2Br is obtained. This compound is partly decomposed by water, yielding mercuric oxide. Concentrated ammonium bromide liberates ammonia from $HgBr_2,2NH_3$, whilst water converts it into NH_2HgBr, which may further decompose according to the equation:

$$9NH_2HgBr = Hg_9N_4Br_6 + 3NH_4Br + 2NH_3;$$

or, if sufficient ammonia is present: $2NH_2HgBr = NHg_2Br + NH_4Br$. Similarly, in ammoniacal solution:

$$2Hg_9N_4Br_6 + 4NH_3 = 9NHg_2Br + 3NH_4Br.$$

It is not found possible to obtain $Hg_9N_4Br_6$ by the action of mercuric bromide on NHg_2Br. Mercuric oxide and ammonium bromide react according to the equation:

$$9HgO + 6NH_4Br = Hg_9N_4Br_6 + 2NH_3 + 9H_2O.$$

In the presence of an excess of mercuric bromide, the following reaction takes place: $3NH_2HgBr + HgBr_2 = 2NH(HgBr)_2 + NH_4Br$. This product is new. It is white, but differs from the other compounds in being sensitive to light. It is not converted into $Hg_9N_4Br_6$ by the action of water. It is formed by the action of ammonium bromide and mercuric bromide on mercuric oxide:

$$3HgO + 2NH_4Br + HgBr_2 = 2NH(HgBr)_2 + 3H_2O.$$

C. H. D.

Colour Suddenly Assumed by Colourless Solutions of Coloured Substances at the Moment of Solidification of the Colourless Solvent. DÉSIRÉ GERNEZ (*Compt. rend.*, 1910, **151**, 272—276; *Ann. Chim. Phys.*, 1910, [viii], 21, 283—288. Compare Abstr., 1903, ii, 428, 481).—The red modification of mercuric iodide behaves like metallic mercury with molten phosphorus (this vol., ii, 707), forming a solution which remains colourless if kept in a superfused condition. If solidification is induced, however, the yellow form is deposited. Solutions of mercuric iodide in formanilide, salol, menthol, thymol, or benzophenone behave in the same way. Solutions in liquid naphthalene, spermaceti, or the higher fatty acids are colourless, but become yellow if rapidly cooled. Such solutions, however, slowly become red if kept below the transition temperature of 126°.

W. O. W.

Scandium. II. RICHARD J. MEYER and HERBERT WINTER (*Zeitsch. anorg. Chem.*, 1910, **67**, 398—417. Compare Meyer, Abstr., 1909, ii, 45; Crookes, *ibid.*, 44; this vol., ii, 714).—The mixture of rare earths obtained from the Zinnwald wolframite contains 56·4% of scandium oxide, whilst direct precipitation with sodium silicofluoride yields a product containing 93·3% of scandium oxide, equivalent to

0·1% of the whole mineral I and II. A similar proportion is found in the wolframite from Sadisdorf, near Schmiedeberg (analysis III).

	WO_3.	FeO.	MnO.	TiO_2 + Ta_2O_5.	PbO + SnO_2.	CaO.	Rare earths.
I.	75·41	9·34	14·00	0·50	0·18	0·55	0·15
II.	—	9·36	14·15	0·47	0·35	0·70	0·15
III.	73·47	15·13	9·81	0·63	0·47	0 54	0·20

Analysis IV represents an ancient tin slag from Zinnwald, containing 0·09% of scandium oxide. The part not estimated is mainly calcium phosphate.

	Metallic Sn.	SnO_2.	SiO_2.	WO_3.	FeO.	MnO.
IV.	6·5	8·6	16·0	30·0	18·4	9·0

Specimens of wiikite examined are free from scandium.

For the separation of thorium from scandium, extraction of the ignited oxides with hydrochloric acid results in complete solution, although thorium oxide is ordinarily insoluble. Hydrogen peroxide also fails to remove thorium, whilst the separation by extracting the oxalates with hydrochloric acid is incomplete. Most of the thorium may be removed by precipitation with iodic acid, and fractional sublimation of the anhydrous chloride also gives good results, scandium chloride being the less volatile.

[With M. SPETER.]—The best separation is obtained by boiling the carbonates with a solution of sodium carbonate, when a sparingly soluble scandium salt separates at a concentration at which thorium remains completely dissolved. The purity of the scandium oxide is tested spectroscopically and by its freedom from radioactivity.

Scandium sodium carbonate has the composition

$$Sc_2(CO_3)_3,4Na_2CO_3,6H_2O,$$

and the *ammonium* salt, $2Sc_2(CO_3)_3,(NH_4)_2CO_3,6H_2O$. A potassium salt is not obtainable under similar conditions. Two precipitations of the double carbonate yield a product of atomic weight 45, which is not changed by further precipitation. Crystallisation of the acetylacetonate from alcohol yields a product of the same atomic weight, thorium remaining in solution. The atomic weight is still 44·9 after six crystallisations, a result higher than that adopted on the basis of Nilson's older determinations. C. H. D.

Preparation and Fusion of Aluminium Nitride. DAFFY WOLK (*Compt. rend.*, 1910, **151**, 318—319. Compare Kohn-Abrest, this vol., ii, 506, 715; Serpek, this vol., ii, 615).—In connexion with the question of priority, the author draws attention to his own communications. Aluminium begins to unite with nitrogen at 820—850°; absorption is rapid at 1000°, but at 1100° decomposition occurs. Ammonia has no specific action on aluminium W. O. W.

Double Bromides of Manganese. FRITZ EPHRAIM and SAMUEL MODEL (*Zeitsch. anorg. Chem.*, 1910, **67**, 376—378).—Manganous bromide has little tendency to form double bromides. Negative results are obtained with potassium, barium, and strontium bromides.

Sodium and ammonium bromides appear to form mixed crystals with manganous bromide.

Calcium manganous bromide, $CaMnBr_4,4H_2O$, forms pink crystals, and readily breaks up into its components. C. H. D.

Complex Compounds of Manganese Salts with Hydroxy-acids. Olof Tamm (*Zeitsch. physikal. Chem.*, 1910, **74**, 496—502). —As Euler and Bolin (Abstr., 1909, i, 863) have shown that the laccase from *Medicago sativa* consists largely of salts of organic hydroxy-acids, the author has investigated the complexes formed with manganese salts by determining the constant of the equation $[Mn(OH)_2]$[hydroxy-acid ion]/[complex ion] $= k$ for different hydroxy-acids at room temperature. The method employed was to shake freshly-precipitated and washed manganous hydroxide with equivalent normal solutions of the sodium salts of the respective acids until equilibrium was reached, and to determine the amount of manganese dissolved. The solubility of the hydroxide in water was also determined; it amounts to $2\cdot10^{-4}$ mol. per litre. From the results, the following values of k were obtained: citric acid, $2\cdot4\times10^{-3}$; tartaric acid, $7\cdot1\times10^{-3}$, and malic acid, $11\cdot6\times10^{-3}$.

It was found, however, that when manganous hydroxide is formed in the presence of the sodium salt of the hydroxy-acid a much greater amount remains dissolved. In the case of sodium citrate, about nine times as much hydroxide remained in solution as when the citrate was shaken with precipitated and washed manganous hydroxide. G. S.

The Spontaneous Decomposition of Permanganates and Permanganic Acid. Anton Skrabal (*Zeitsch. anorg. Chem.*, 1910, **68**, 48—51).—The author considers that the evolution of oxygen in the decomposition of permanganates is chiefly due to the reaction $Mn^{II} + Mn^{VII} \longrightarrow Mn^{III} \longrightarrow Mn^{II} + O_2$ (Abstr., 1905, ii, 804; 1906, ii, 658), whilst Sirkar and Dutta (Proc., 1909, **25**, 249; *Zeitsch. anorg. Chem.*, 1910, **67**, 225) regard it as arising from the reaction $Mn^{IV} \longrightarrow Mn^{II} + O_2$. The velocity of the latter reaction is, however, very small, whilst the evolution of oxygen is most rapid during, and not after, the reduction of the permanganate by manganous salt or by organic matter. C. H. D.

Action of Mixtures of Carbon Monoxide or Carbon Dioxide with Hydrogen on Oxides of Iron. Armand Gautier and P. Clausmann (*Compt. rend.*, 1910, **151**, 355—359. Compare Abstr., 1906, ii, 538; this vol., ii, 607, 709).—A mixture of carbon monoxide (3 mols.) and hydrogen (1 mol.) passed over heated magnetic oxide of iron converts it into a mixture of the carbide, $Fe_{12}C$, with ferric oxide and free carbon. The product yields methane and hydrogen when heated in a vacuum at 100°. Similar results are obtained when carbon monoxide and hydrogen are passed over freshly-reduced iron at 1250°; the mixture of gases evolved contains small amounts of methane.

Carbon monoxide and hydrogen saturated with water vapour were passed over iron at 250—300°. The aqueous distillate contained a

trace of formaldehyde, and held in suspension colourless, highly refractive spangles. Extraction with ether resulted in the isolation of a substance resembling vaselin in general properties. After a time it partly solidified, and then had m. p. 35—36°; on heating it evolved a fatty odour.

The bearing of these observations on the formation of petroleum is discussed. W. O. W.

Negative Ferric Hydroxide. I. The Preparation and Properties of Negative Ferric Hydroxide. HERMANN W. FISCHER (*Biochem. Zeitsch.*, 1910, **27**, 223—237).—The investigations were undertaken with the view of finding an antidote to arsenic poisoning, such as occurs in treatment with atoxyl and other similar drugs. The colloidal iron hydroxide, as ordinarily prepared, has a positive charge, and as serum proteins are negatively charged, such a preparation when injected can lead to embolisms. If sodium hydroxide be added to ferric chloride solution containing glycerol, at a certain point precipitation takes place, and the solution remains neutral; on further addition of the base, the precipitate redissolves. This "protective" action of glycerol in causing colloidal solution is characteristic of other hydroxyl-containing substances, such as lævulose, mannitol, etc., and the author summarises the literature on this subject. The "protection" is probably of chemical nature. The weak basic ferric hydroxide hydrosols form a transparent, ruby-red solution, which can be made to contain a high percentage of metal. On prolonged dialysis, the solution forms a gel, which will liquefy on addition of alkali or "protective" substance. A gel containing only 1% iron is quite firm. The author points to certain analogies in the properties of iron in this form to the iron in hæmoglobin. S. B. S.

Negative Ferric Hydroxide. II. Ferric Hydroxide and Serum. HERMANN W. FISCHER (*Biochem. Zeitsch.*, 1910, **27**, 238—245).—Positively-charged ferric hydroxide forms precipitates with the negatively-charged serum proteins. The negative colloidal ferric hydroxide (see preceding abstract) was found to be very toxic to rabbits after intravenous injection. If such hydrosols contain excess of alkali and sufficient amount of "protective" substance, they will not form precipitates with serum, and are not immediately toxic. They act, however, toxically (if intravenously injected) after some hours. A figure is given of an apparatus for rapid dialysis.

S. B. S.

Chromic Chloride. III. NIELS BJERRUM (*Zeitsch. physikal. Chem.*, 1910, **73**, 724—759. Compare Abstr., 1907, ii, 554, 622).—There are two distinct classes of basic chromium compounds, the manifestly basic, which are formed momentarily in aqueous solution at the ordinary temperature, and the latent basic, which are only formed slowly in aqueous solution. The present paper is concerned with the manifestly basic compounds formed from the bluish-violet chromic chloride hexahydrate. The degree of hydrolysis of solutions of the chloride in the presence of varying proportions of alkali was determined with the hydrogen electrode in the usual way.

It is shown that, contrary to the statement of Sand and Grammling (Abstr., 1908, ii, 293), the chloride itself is unimolecular. On progressive hydrolysis, it gives rise to two soluble, manifestly basic chlorides, $Cr(OH)Cl_2$ and $Cr(OH)_2Cl$, and an insoluble, grey-green, manifestly basic hydroxide. The compound $Cr(OH)_2Cl$ is never present in any large proportion, and the hydroxide is formed only on addition of alkali. The hydroxyl in these compounds is united directly to the chromium atom. The amounts of water associated with the molecules have not been determined, but the respective formulæ are probably as follows: $[Cr(H_2O)_5(OH)]Cl_2$; $[Cr(H_2O)_4(OH)_2]Cl$; $Cr(H_2O)_3(OH)_3$. The relative amounts of these substances in solution under varying conditions are given by the following equations:

$$k_1 = [Cr(OH)Cl_2][x]/[CrCl_3]$$

$= 0{\cdot}22$ at 0°, $0{\cdot}62$ at 17°, and $0{\cdot}98$ at 25°.

$$k_2 = [Cr(OH)_2Cl][x]/[Cr(OH)Cl_2]$$

$= 0{\cdot}0025$ (in $N/10$-solution of potassium chloride) at 0° and $0{\cdot}0059$ at 17°. $k_3 = Cr(OH)_2Cl{:}x^2$ is 36,000 in $N/10$-potassium chloride solution at 0° and 10,200 at 17°. In the above equations, x is the concentration of free acid, and the unit of concentration is 1/10,000 molar throughout.

From the displacement of the equilibria with temperature, the heats of reaction are calculated in the usual way. The reaction $Cr(OH)_3 + 3HCl = CrCl_3 + 3H_2O$ gives out 21,200 cal., the reaction $Cr(OH)_2Cl + HCl = Cr(OH)Cl_2 + H_2O$ at least 8060 cal., and the reactions $Cr(OH)Cl_2 + HCl = CrCl_3 + H_2O$ gives 9600 cal.

Freshly precipitated chromic hydroxide is a well-defined chemical compound, the solubility product of which is $4{\cdot}2 \times 10^{-16}$ at 0° and 54×10^{-16} at 17° in 1/10,000 molar units. G. S.

Complex Metal Ammonias. X. ALFRED WERNER (*Annalen*, 1910, **375**, 1—144. Compare Abstr., 1909, ii, 49).—The author's investigations on the complex metal ammonias have now reached such a stage that a summary of the results obtained can be given. Such a summary of the complex cobalt ammonias is given in the present paper, together with the results of hitherto unpublished investigations; there is also a detailed account of the methods used for deducing the constitution of these complex compounds.

The general results arrived at may be briefly summarised as follows:

(A). *Theoretical Results in Connexion with Valency.*—(1) The oxygen of an hydroxyl group linked to one cobalt atom can enter into combination with a second cobalt atom, thus: $Co\text{—}\overset{H}{O}\cdots Co$. (2) The nitrogen of an amino-group can act similarly, thus: $Co\text{—}\overset{H_2}{N}\cdots Co$. This linking is very stable, and plays the chief part in the formation of complex cobalt ammonias. (3) The oxygen molecule can form the connecting link between two cobalt atoms, $Co{\cdot}O_2{\cdot}Co$; these atoms may be both tervalent (dicobalti-compounds), or the one tervalent and the other quadrivalent (cobalticobalt compounds). (4) In the complex cobalt ammonias two cobalt atoms are never directly linked one with the other. (5) If two cobalt atoms are already linked by the ·OH

or $\cdot NH_2$ groups, the following atomic groups may also form additional bridged linkings: NO_2; SO_2; $O\cdot COMe$; $O\cdot COR$; C_2O_4. (6) Two cobalt atoms may be linked to each other by one, two, or three bridged linkings. The following combinations have been proved to exist: (*a*) Dicobalt ammonias: (*α*) with one bridged linking, $Co\cdot X\cdot Co$, where $X = NH_2$ or O_2; (*β*) with two bridged linkings, $\mathrm{Co}\begin{smallmatrix}\cdot X\cdot\\ \cdot Y\cdot\end{smallmatrix}\mathrm{Co}$, where $X = \cdot OH$ or $\cdot NH_2$, and $Y = OH, NH_2, O_2, NO_2$; also, $\mathrm{Co}\begin{smallmatrix}\cdot NH_2\cdot\\ \cdot\ Y\ \cdot\end{smallmatrix}\mathrm{Co}$, where $Y = SO_4$ or C_2O_4; (*γ*) with three bridged linkings, $\mathrm{Co}\begin{smallmatrix}\cdot NH_2\cdot\\ \cdot OH\cdot\\ \cdot\ X\ \cdot\end{smallmatrix}\mathrm{Co}$, where $X = OH, NO_2, O\cdot COMe$, or O_2; $\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\\ \cdot\ Y\ \cdot\end{smallmatrix}\mathrm{Co}$, where $Y = OH, NO_2$, or $O\cdot COMe$; and $\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot NO_2\cdot\\ \cdot NO_2\cdot\end{smallmatrix}\mathrm{Co}$. (*b*) Tricobalt ammonias: (*α*) with four bridged linkings, $\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}$; (*β*) with six bridged linkings, $\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}$. (*c*) Tetra-cobaltammonias with six bridged linkings, $\mathrm{Co}\left(\begin{smallmatrix}\cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}\right)_3$.

(7) In all the compounds investigated the maximum co-ordination number of ter- and quadri-valent cobalt is six, as with the simple cobalt ammonias.

(B). *New Results with Respect to Inorganic Isomerism.*—Three kinds of isomerism are distinguished: (1) *Polymerism or nuclear-polymerism*; for example, *hexamminetrioldicobalti*-salts,

$$\left[(H_3N)_3\mathrm{Co}\begin{smallmatrix}\cdot OH.\\ \cdot OH\cdot\\ \cdot OH\cdot\end{smallmatrix}\mathrm{Co}(NH_3)_3\right]X_3,$$

and *dodeca-amminehexoltetracobalti*-salts, $\left[\mathrm{Co}\left(\begin{smallmatrix}OH\cdot\\ OH\cdot\end{smallmatrix}\mathrm{Co}(NH_3)_4\right)_3\right]X_6$.

(2) *Valency isomerism*; for example, *tetraethylenediamine-μ-aminoperoxo-cobalticobalte* salts, $\left[en_2\mathrm{Co}\lessdot\begin{smallmatrix}-O_2-\\ NH_2\end{smallmatrix}\gtrdot\mathrm{Co}\,en_2\right]X_4$, and *tetraethylenediamine-μ-ammoniumperoxocobalticobalte* salts, $\left[\begin{smallmatrix}en_2\mathrm{Co}\lessdot\begin{smallmatrix}-O_2-\\ NH\end{smallmatrix}\gtrdot\mathrm{Co}\,en_2\\ \vdots\\ HX\end{smallmatrix}\right]X_3$.

The salts of the former series are green and of neutral reaction, those of the latter being red and of acid reaction. (3) *Co-ordinative position-isomerism*, which may be compared with the organic isomerism: $CH_3\cdot CHX_2$ and $CH_2X\cdot CH_2X$; for example, symmetrical and asymmetrical *dichlorohexammine-μ-aminoperoxocobalticobalte chloride*,

$$\left[\begin{smallmatrix}Cl\\ (H_3N)_3\end{smallmatrix}\mathrm{Co}\begin{smallmatrix}\cdot NH_2\cdot\\ \cdot\ O_2\ \cdot\end{smallmatrix}\mathrm{Co}\begin{smallmatrix}Cl\\ (NH_3)_3\end{smallmatrix}\right]Cl_2 \text{ and } \left[(H_3N)_4\mathrm{Co}\begin{smallmatrix}\cdot NH_2\cdot\\ \cdot\ O_2\ \cdot\end{smallmatrix}\mathrm{Co}\begin{smallmatrix}Cl_2\\ (NH_3)_2\end{smallmatrix}\right]Cl_2.$$

Both series of salts are green and resemble each other in appearance, but chemically they are very different.

Decammine-μ-aminodicobalti-salts, $[(H_3N)_5Co\cdot NH_2\cdot Co(NH_3)_5]X_5$ (compare Abstr., 1909, ii, 49). A new method of preparaton is given. When a freshly prepared solution of chloroaquo-octammine-μ-aminodicobalti-chloride is treated with concentrated nitric acid a greyish-violet precipitate of *chloronitrato-octammine-μ-aminodicobalti-nitrate*, $\left[{}^{Cl}_{(H_3N)_4}Co\cdot NH_2\cdot Co^{NO_3}_{(NH_3)_4}\right](NO_3)_4$, separates. The dry salt is dissolved in liquid ammonia, and, after evaporating off the ammonia, the residue is covered with water and heated on the water-bath until the greater part has dissolved. The insoluble part is filtered from the hot solution and recrystallised from water containing acetic acid, when long, bluish-red needles of decammine-μ-aminodicobalti-nitrate are obtained.

[With Franz Salzer.]—The following compounds derived from the octammine-μ-amino-ol-dicobalti-salts (compare Abstr., 1908, ii, 42) are described.

Chloroaquo-octammine-μ-amino ol-dicobalti-salts, YX_4, where

$$Y=\left[{}^{H_2O}_{(H_3N)_4}Co\cdot NH_2\cdot Co^{Cl}_{(NH_3)_4}\right].$$

To prepare the *chloride*, $YCl_4,4H_2O$, 10 grams of crude sulphato-octammine-μ-aminodicobalti-nitrate (Abstr., 1908, ii, 42) are covered with 150 c.c. of hydrochloric acid (D = 1·19) and kept at room temperature, the mixture being well shaken at intervals. The sulphatonitrate dissolves, the ·OH bridged linking being destroyed, and then crystals of the chloride are deposited. After twenty-four hours they are collected, dissolved in cold water, and re-precipitated by concentrated hydrochloric acid; brownish-violet needles, readily soluble in water, giving an acid solution. The concentrated solution deposits, after a time, prismatic, reddish-brown crystals of *octammine-μ-amino-ol-dicobalti-chloride*, $\left[(H_3N)_4Co{<}{}^{NH_2}_{OH}{>}Co(NH_3)_4\right]Cl_4 + HCl$. On long boiling with concentrated hydrochloric acid the chloride (YCl_4) is decomposed completely into pentammine- and tetrammine-cobalti-salts. The freshly prepared aqueous solution gives characteristic precipitates with solutions of chlorplatinic acid, mercuric chloride, and potassium iodide. Dilute sulphuric acid produces a quantitative precipitation of the *sulphate*, $Y(SO_4)_2,H_2O$; pale reddish-violet crystals. Sodium dithionate gives a voluminous, greyish-violet, crystalline precipitate of the *dithionate*, $Y(S_2O_6)_2$.

Chlorothiocyanato-octammine-μ-aminodicobaltithiocyanate,

$$\left[{}^{NCS}_{(H_3N)_4}Co\cdot NH_2\cdot Co^{Cl}_{(NH_3)_4}\right](SCN)_3,$$

is obtained as a brownish-red, crystalline precipitate when a saturated solution of the corresponding chloride is treated with a saturated solution of ammonium thiocyanate. *Chloronitrato octammine-μ-amino-dicobaltinitrate*, $\left[{}^{Cl}_{(H_3N)_4}Co\cdot NH_2\cdot Co^{NO_3}_{(NH_3)_4}\right](NO_3)_3$, is prepared by dissolving 3 grams of chloroaquo-octammine-μ-aminodicobalti-chloride in 50 c.c. of ice-cold water, filtering, and adding 15 c.c. of concentrated

nitric acid. A reddish-violet precipitate is produced, which rapidly changes to a brownish-violet colour. The fresh solution gives no precipitate with silver nitrate at first, but on standing silver chloride is formed. From the warm solution, dilute sulphuric acid precipitates octammine-μ-amino-ol-dicobalti-sulphate.

Bromoaquo-octammine-μ-aminodicobalti-salts, YX_4, where

$$Y = \left[{}^{Br}_{(NH_3)_4}Co\cdot NH_2\cdot Co^{OH_2}_{(NH_3)_4} \right].$$

To obtain the *bromide*, YBr_4, octammine-μ-amino-ol-dicobalti-sulphate (Abstr., 1908, ii, 42) is triturated with concentrated hydrobromic acid. The resulting product is washed free from acid with alcohol, dissolved in ice-cold water, the solution filtered, and then precipitated with concentrated hydrobromic acid; dark brown, flat needles. The aqueous solution is acid, and after a time deposits red, prismatic crystals of octammine-μ-amino-ol-dicobalti-bromide. The *sulphate*, $Y(SO_4)_2,H_2O$, is prepared by adding a freshly prepared solution of the bromide in ice-cold water to dilute sulphuric acid; dark brown crystals, almost insoluble in water.

Sulphato-octammine-μ-aminodicobalti-salts, YX_3, where

$$Y = \left[(H_3N)_4Co\Big\langle{}^{NH_2}_{SO_4}\Big\rangle Co(NH_3)_4 \right]$$

The salts of this series were formerly described as *hydrosulphatoimido-octamminedicobalti*-salts (Abstr., 1898, ii, 224). The best method of preparation is now found to be as follows:—Solutions of pure octammine-μ-amino-ol salts are heated with sulphuric acid. The pale red sulphate is first precipitated, and dissolves again to a reddish-violet solution, from which the required salts can be precipitated by suitable reagents. The *acid sulphate*, $Y(SO_4)(HSO_4)$, results when 3 grams of octammine-μ-amino-ol-dicobalti-chloride are heated with 10 c.c. of water and 2 c.c. of concentrated sulphuric acid until a clear violet solution is obtained. Purplish-violet, prismatic leaflets separate on cooling. The *bromide*, YBr_3,H_2O, and *nitrate*, $Y(NO_3)_3$, result when concentrated hydrobromic acid and nitric acid respectively are added to a solution of the sulphate. The nitrate forms violet-red crystals.

[With FRANZ SALZER and M. PIEPER.]—*Octammine-μ-aminonitrodicobalti*-salts, YX_4 where $Y = \left[(H_3N)_4Co\Big\langle{}^{NH_2}_{NO_2}\Big\rangle Co(NH_3)_4 \right]$. The nitrate, chloride, and sulphate have previously been described as hydronitritoimido-octamminedicobalti-salts (Abstr., 1898, ii, 223), but since then their constitution has been fully investigated. The salts are amongst the most stable of the complex cobalt ammonias. The nitrate, $Y(NO_3)_4,H_2O$, is the most convenient starting point for the preparation of the other salts. New methods of preparation are as follows: (1) A concentrated solution of sodium nitrite is added drop by drop to a mixture of the green octammine-μ-aminoperoxocobalticobalte nitrate with excess of concentrated nitric acid. The green nitrate changes to orange-yellow crystals, which are collected and recrystallised from water containing nitric acid. (2) Sodium nitrite is added to a warm concentrated aqueous solution of octammine-μ-amino-ol-dicobalti-chloride until a yellowish-brown colour is obtained. The nitrate separates on cooling, after the addition of nitric acid. (3) A con-

centrated, fresh solution of chloroaquo-octammine-μ-aminodicobalti-chloride is treated with sodium nitrite and warmed until the colour becomes orange. The addition of concentrated nitric acid then gives a precipitate of the required nitrate.

With ammonia the nitrate, $Y(NO_3)_4$, does not lose one molecule of acid with the formation of imino-salts. From a solution containing pyridine, it crystallises with one molecule of pyridine, the base not being contained in the complex. Besides the chloride, YCl_4,H_2O (*loc. cit.*), there is also a *chloride*, $YCl_4,4H_2O$, which is obtained when the ordinary chloride is crystallised from a solution containing pyridine. The *bromide*, $YBr_4,3H_2O$, is obtained by treating a solution of the sulphate with the calculated quantity of barium bromide, and precipitating the filtrate from the barium sulphate with hydrobromic acid; brownish-red, rhombic prisms or plates. The *iodide*, YI_4,H_2O, is obtained from the nitrate by precipitation with potassium iodide; large, dark red prisms. When recrystallised from water containing pyridine it contains $4H_2O$.

[With ADOLF GRÜN.]—*Octammine-μ-aminoperoxocobalticobalte* salts, YX_4, where $Y = \left[(H_3N)_4\overset{III}{Co}\begin{smallmatrix}NH_2\\ O_2\end{smallmatrix}\overset{IV}{Co}(NH_3)_4\right]$. These were formerly described as oxodi-imido-octamminedicobalti-salts (Abstr., 1898, ii, 223), but further investigation has shown them to have the constitution given above. Reducing agents, such as hydriodic acid, give octammine-μ-amino-ol-dicobalti-salts. When warmed with concentrated sulphuric acid, one and a-half atoms of oxygen are liberated for every two atoms of cobalt, corresponding with the change from quadri- to ter-valent cobalt. On further strongly heating, one-third atom of nitrogen is evolved for each atom of cobalt, corresponding with the change from ter- to bi-valent cobalt.

The *nitrate*, YX_4, is obtained by treating the green sulphate contained in Vortmann's sulphate (Abstr., 1908, ii, 42) with nitric acid; it forms dark green, prismatic crystals, which are anhydrous. A hydrated nitrate could not be obtained (compare Abstr., 1908, ii, 223). The aqueous solution rapidly decomposes, cobalt oxide being deposited. The *sulphate*, $Y(SO_4)_2,2H_2O$, is precipitated when aqueous solutions of other salts are treated with dilute sulphuric acid; greenish-grey, prismatic crystals. The *chloride*, YCl_4,H_2O, and the *bromide*, YBr_4,H_2O, are obtained by triturating the sulphate with concentrated hydrochloric and hydrobromic acids respectively, and forms dark green crystals. Sodium dithionate precipitates the *dithionate*, $Y(S_2O_6)_2$, from an aqueous solution of the nitrate containing acetic acid.

The central group, $Co\begin{smallmatrix}NH_2\\ O_2\end{smallmatrix}Co$, of this series is very stable. By warming the nitrate with 10% ethylenediamine all the ammonia molecules can be replaced by ethylenediamine. If the resulting solution is then neutralised with nitric acid at the ordinary temperature, a green salt is obtained; when the neutralisation is carried out at low temperatures a red salt is obtained. These salts only differ in their molecular composition, in that the former is anhydrous, whereas the latter contains 2 mols. of water of crystallisation. The aqueous solution of the former is neutral, whereas that of the latter is acid. On

warming a nitric acid solution of the red salt, it changes into the green salt. The green salt is *tetraethylenediamine-μ-aminoperoxocobalticobalte nitrate*, $Y(NO_3)_4$, where $Y = \left[en_2Co<^{NH_2}_{O_2}>Co\,en_2 \right]$. During the preparation some decomposition also takes place, with the formation of *triethylenediaminecobalti*-salts. Reduction of the nitrate with sodium iodide or potassium thiocyanate gives precipitates of the corresponding tetraethylenediamine-μ-amino-ol-dicobalti-iodide and thiocyanate. The *bromide*, $YBr_4,5H_2O$, is precipitated as yellowish-green crystals when ammonium bromide is added to a cold saturated solution of the nitrate.

The red salt is *tetraethylenediamine-μ-ammoniumperoxocobalticobalte nitrate*, $[Y{\cdot}HNO_3](NO_3)_3,2H_2O$, where $Y = \left[en_2Co<^{O_2}_{NH}>Co\,en_2 \right]$. The *bromide*, $[Y{\cdot}HBr]Br_3,3H_2O$, obtained by precipitating a solution of the red nitrate with potassium bromide, forms red crystals giving a brown solution in water, which is first turned red and then green by mineral acids. A bromide containing $1H_2O$ can also be obtained.

Under the action of ammonia both the green and the red salts lose a molecule of acid, forming *tetraethylenediamine-μ-iminoperoxocobalticobalte* salts. The *iodide*, $\left[en_2Co<^{NH}_{O_2}>Co\,en_2 \right] I_2,5H_2O$, is readily obtained from tetraethylenediamine-μ-aminoperoxocobalticobalte bromide by triturating the mixture with ammonia and sodium iodide. It is purified by solution in water and re-precipitation with potassium iodide; small, brown needles. On shaking the aqueous solution with silver chloride, a solution of the *chloride* results, but crystals cannot be obtained. If hydrochloric acid is added to this solution, it first becomes red, the ammoniumperoxo-salt being formed, and then green, isomerisation to the aminoperoxo-salt taking place. The solution of the iodide gives characteristic precipitates with potassium platinichloride and with potassium aurichloride. Silver nitrate first gives a precipitate of silver iodide, and then an *additive compound* of the nitrate with silver nitrate, $3\left[en_2Co<^{O_2}_{NH}>Co\,en_2 \right](NO_3)_3 + 5AgNO_3$; dark brown crystals. Similar addition compounds may be obtained with copper nitrate (apple-green crystals) and with mercuric chloride (brilliant red crystals).

Both the red and the green salts give rise to *tetraethylenediamine-μ-amino-ol-dicobalti*-salts when reduced by means of acetic acid and potassium iodide. The *iodide*, YI_4, where $Y = \left[en_2Co<^{NH_2}_{OH}>Co\,en_2 \right]$, is readily obtained from the aminoperoxodicobalt nitrate in this way. The periodide which is first formed is destroyed with sodium thiosulphate, and the iodide separates as light red crystals from the resulting solution. The *bromide*, $YBr_4,4H_2O$, may be obtained by adding ammonium bromide to the solution of the iodide; dark red crystals.

When an aqueous solution of tetraethylenediamine-μ-aminoperoxodicobalt nitrate is treated with glacial acetic acid and excess of potassium thiocyanate, red crystals of the thiocyanate are obtained.

If these are oxidised with concentrated nitric acid, the resulting solution precipitated with alcohol, and ammonium bromide added to an aqueous solution of the precepitate, red crystals of *sulphatotetraethylenediamine-μ-aminodicobalti-bromide*, $\left[en_2Co{<}^{NH_2}_{SO_4}{>}Co\,en_2\right]Br_3$, are obtained.

[With E. KINDSCHER.]—*Octamminedioldicobalti*-salts, YX_4, where $Y = \left[(H_3N)_4Co{<}^{OH}_{OH}{>}Co(NH_3)_4\right]X_4$. The chloride, bromide, nitrate, thiocyanate, dithionate, and sulphate of this series have been described previously (Abstr., 1907, ii, 965). The following salts have all been prepared from an aqueous solution of the chloride by double decomposition with soluble alkali salts of the various acids. *Iodide*, $YI_4,2H_2O$, dark violet crystals; *chlorate*, $Y(ClO_3)_4$, crimson crystals; *bromate*, $Y(BrO_3)_4$, ruby-red crystals; *iodate*, $Y(IO_3)_4$, bright violet crystals; *oxalate*, $Y(C_2O_4)_2,2H_2O$, ruby-red crystals; *chromate*, $Y(CrO_4)_2$, light brown, earthy precipitate; *phosphate*, $Y(HPO_4)_2,6H_2O$, rose-red crystals; *platinochloride*, $Y(PtCl_4)_2$, red crystals; *platinichloride*,

$$Y(PtCl_6)_2,6H_2O,$$

copper-red needles; *aurichloride*, $Y(AuCl_4)_4,4H_2O$, red crystals; *silicofluoride*, $Y(SiF_6)_2$, light violet precipitate.

[With JOS. RAPIPORT.]—*Tetraethylenediamine-diol-dicobalti*-salts, YX_4, where $Y = \left[en_2Co{<}^{OH}_{OH}{>}Co\,en_2\right]$. The salts of this series were prepared from *cis*-hydroxoaquodiethylenediaminecobaltidithionate,

$$\left[{}^{HO}_{H_2O}Co\,en_2\right]S_2O_6$$

(Abstr., 1907, i, 189), for which a new method of preparation from hexaethylenediaminehexoltetracobalti-nitrate (Abstr., 1907, i, 482) is given. By the action of concentrated hydrochloric acid on the hexolnitrate, crystals of *cis*-diaquodiethylenediaminecobalt chloride are obtained. On treating an aqueous solution of these crystals with pyridine and sodium dithionate, crystals of the *cis*-hydroxoaquodiethylenediaminecobaltidithionate are readily formed. When this compound is heated to constant weight at 100—110°, water is lost, with the formation of *tetraethylenediamine-diol-dicobaltidithionate*, $Y(S_2O_6)_2$. The *bromide*, $YBr_4,4H_2O$, may be obtained from the dithionate by triturating with ammonium bromide and water, and forms reddish-violet needles, which lose $2H_2O$ at 100°, or on keeping over concentrated sulphuric acid. The *thiocyanate*, $Y(SCN)_4,3H_2O$, forms a purple, crystalline precipitate when potassium thiocyanate is added to a solution of the bromide. Under similar conditions, sodium nitrate gives purple crystals of the *nitrate*, $Y(NO_3)_4$.

Both the octammine- and the tetraethylenediamine-diol-dicobalti-salts are readily decomposed by concentrated hydrochloric or hydrobromic acids, giving rise to a mixture of *cis*-diaquo- and *cis*-dichloro-salts. This reaction is of use in determining the configuration of stereoisomeric cobalt ammonias.

In the preparation of *cis*-dichlorotetraminecobalti-chloride (violeochloride, $[Cl_2Co(NH_3)_4]Cl$) from octammine-diol-dicobalti-chloride, the crude substance sometimes assumes a superficial red colour when dried

over phosphoric oxide. The conditions governing this change are not known, but if the partly changed salt is dissolved in water and sodium dithionate added after half an hour, orange-yellow crystals of *octammine-µ-diaminodicobaltidithionate*, $Y(S_2O_6)_2$, where

$$Y = \left[(NH_3)_4Co{<}^{NH_2}_{NH_2}{>}Co(NH_3)_4 \right],$$

are precipitated. On rubbing these crystals with ammonium bromide and a little water, red crystals of the *bromide*, $YBr_4,4H_2O$, are obtained.

[With J. FÜRSTENBERG.]—Melanochloride (Abstr., 1898, ii, 226) was used as the starting point for the following series of salts. A new and quicker method of preparation of this chloride is described. A mixture of 650 grams of cobalt chloride with 400 c.c. of water and 2 litres of 25% ammonia is heated to boiling, filtered from the precipitated cobalt oxide, and exposed to the air for forty-eight hours. The resulting brownish-red solution is filtered from the crystals which have deposited, and mixed with 3 litres of concentrated hydrochloric acid. The resulting brownish-red precipitate is quickly collected and extracted with cold water until it becomes pure grey in colour and the wash water is coloured a brownish-violet. One kilo. of cobalt chloride gives about 60 grams of melanochloride.

Diaquohexammine-µ-amino-ol-dicobalti-nitrate,

$$\left[{}^{H_2O}_{(H_3N)_3}Co{<}^{NH_2}_{OH}{>}Co^{OH_2}_{(NH_3)_3} \right](NO_3)_4 + 2H_2O.$$

Twenty grams of melanochloride are triturated with a slightly acid solution of 36 grams of silver nitrate in 60 c.c. of water, and the mixture heated to 50° for some time. The silver chloride is collected and heated at 80° with separate quantities of 60 c.c. of very weak nitric acid until it is colourless. To the united red extracts is added alcohol until incipient crystallisation; on cooling in a freezing mixture, red crystals of the nitrate separate. After solution in water and re-precipitation with concentrated nitric acid, garnet-red, flat, quadratic prisms are obtained. The aqueous solution is acid.

Hexammine-µ-amino-diol-dicobalti-salts, YI_3, where

$$Y = \left[(H_3N)_3Co \begin{matrix} NH_2 \\ OH \\ OH \end{matrix} Co(NH_3)_3 \right],$$

give neutral aqueous solutions. The *iodide*, YI_3, is precipitated by the addition of solid potassium iodide to a solution of diaquohexammine-µ-amino-ol-dicobalti-nitrate; brownish-red needles. The *bromide*, YBr_3,H_2O, results when ammonium bromide is used instead of potassium iodide; it may also be obtained from the chloride by treatment with silver bromide; dark red needles. The *chloride*,

$$YCl_3,H_2O,$$

is prepared from the iodide or bromide by means of silver chloride; bright red needles. The *nitrate*, $Y(NO_3)_3,2H_2O$, results from the interaction of the iodide and silver nitrate; small red crystals.

Nitratoaquohexammine-µ-amino-ol-dicobalti-salts, YX_3, where

$$Y = \left[{}^{H_2O}_{(H_3N)_3}Co{<}^{NH_2}_{OH}{>}Co^{NO_3}_{(NH_3)_3} \right].$$

The nitrate, $Y(NO_3)_3,2H_2O$ (compare Abstr., 1899, ii, 658), is best

prepared as follows: One gram of diaquohexammine-μ-amino-ol-dicobalti-nitrate is dissolved in 7 c.c. of hot water to which a few drops of nitric acid have been added. To the cooled solution, 18 c.c. of concentrated nitric acid are added; after a few minutes, yellowish-brown, flat needles of the required nitratonitrate separate. The addition of concentrated hydrochloric acid to a cold solution of the nitrate precipitates yellowish-brown, flat needles of the *chloride*, YCl_3,H_2O. With hydrobromic acid or ammonium bromide, flesh-coloured, flat needles of the *bromide*, YBr_3,H_2O, are obtained.

[With FRL. SIGNE MALMGREN.]—When nitratoaquohexammine-μ-amino-ol-dicobalti-nitrate is dissolved in liquid ammonia and the ammonia allowed to evaporate, a reddish-brown residue is obtained. If this is extracted with cold water and ammonium sulphate added to the extracts, an insoluble sulphate is precipitated, from which a soluble nitrate may be obtained by treatment with ammonium nitrate. The solution of the nitrate gives, with ammonium bromide a red precipitate of *octammine-μ-amino-ol-dicobalti-bromide.* This reaction proves the presence of a μ-amino-bridged linking in the hexammine compound.

[With J. FÜRSTENBERG.]—On adding concentrated hydrochloric acid to a warm solution of diaquohexammine-μ-amino-ol-dicobalti-nitrate, microscopic, dark violet, hexagonal leaflets are precipitated. When dried at 60—65°, it consists of *tetrachlorohexammine-μ-aminodicobalti-chloride*, $\left[{}^{Cl_2}_{(H_3N)_3}Co\cdot NH_2\cdot Co^{Cl_2}_{(NH_3)_3}\right]Cl$. When dried at the ordinary temperature only three of the chlorine atoms are non-ionic, the salt then being *trichloroaquohexammine-μ-aminodicobalti-chloride*,

$$\left[{}^{Cl_2}_{(H_3N)_3}Co\cdot NH_2\cdot Co\begin{matrix}Cl\\OH_2\\(NH_3)_3\end{matrix}\right]Cl_2,$$

that is, the pure melanochloride. When this salt is triturated with concentrated nitric acid, dissolved in cold water, and the solution immediately precipitated with nitric acid, violet-black crystals of *trichloronitratohexammine-μ-aminodicobalti-nitrate*,

$$\left[{}^{Cl_2}_{(H_3N)_3}Co\cdot NH_2\cdot Co\begin{matrix}Cl\\NO_3\\(NH_3)_3\end{matrix}\right]NO_3,$$

are obtained.

Tetrabromohexammine-μ-aminodicobalti-salts, YX, where Y = $\left[{}^{Br_2}_{(H_3N)_3}Co\cdot NH_2\cdot Co^{Br_2}_{(NH_3)_3}\right]$. The *bromide*, $YBr,2H_2O$, is formed on warming the aqueous solution of hexammine-μ-amino-diol-dicobalti-bromide with concentrated hydrobromic acid; brownish-yellow, crystalline powder, which becomes anhydrous at 70—80°. The *nitrate*, $YNO_3,2H_2O$, resembles the bromide in appearance, and is prepared from the latter by trituration with nitric acid.

The salts of the trichloro-, tetrachloro-, and tetrabromo-series are all re-converted into tetraquohexamminedicobalti-nitrate by digestion with a slightly acid solution of silver nitrate.

Dichlorohexammine-μ-aminonitrodicobalti-salts, YX_2, where Y = $\left[{}^{Cl}_{(H_3N)_3}Co{<}^{NH_2}_{NO_2}{>}Co^{(NH_3)_3}_{Cl}\right]$. In these compounds the nitro-

group is very firmly combined. The *chloride*, YCl_2,H_2O, is obtained by warming 1 gram of tetraquohexammine-μ-amino-ol-nitrate with 0·25 gram of sodium nitrite and a little water. To the resulting orange-coloured solution, concentrated hydrochloric acid is added, when nitrous fumes are evolved and the chloride deposited as red flakes. It is identical with the hydronitritoimidohexamminedicobalti-chloride previously prepared from melanochloride (Abstr., 1898, ii, 226). The *nitrate*, $Y(NO_3)_2$, is prepared by triturating the chloride with concentrated nitric acid; reddish-brown, crystalline powder.

[With J. FÜRSTENBERG.]—*Hexammine-μ-amino-ol-acetatodicobalti*-salts, YX_3, where $Y = \left[(H_3N)_3Co\begin{matrix}\diagup NH_2 \diagdown \\ OH \longrightarrow \\ \diagdown \underset{\substack{| \\ Me}}{OCO} \diagup\end{matrix}Co(NH_3)_3\right]$. In these compounds the acetic acid residue is very firmly combined. Their properties are very different from the ol-compounds, from which they are derived, as they no longer show the so-called melano-reaction. Their aqueous solutions are neutral. The *iodide*, YI_3, is prepared by warming a solution of diaquohexammine-μ-amino-ol-dicobalti-nitrate with acetic acid, and then adding excess of potassium iodide. On cooling, it is deposited as vivid-red, prismatic needles or plates. The *bromide*, YBr_3, and the *chloride*, YCl_3, are obtained from the iodide by treatment with silver bromide and chloride respectively; bright red needles. The *nitrate*, $Y(NO_3)_3$, results from the interaction of the iodide and silver nitrate. With potassium platinochloride, the solution of the chloride gives bright red crystals of the *platinochloride*, $Y_2(PtCl_4)_3$.

When solutions of these salts are precipitated with nitric acid they do not give the corresponding nitrate, but the nitrate of the *diaquo-hexammine-μ-aminoacetatodicobalti*-series, YX_4, where

$$Y = \left[\begin{matrix}H_2O \\ (H_3N)_3\end{matrix}Co\begin{matrix}\diagup NH_2 \diagdown \\ \diagdown \underset{\substack{| \\ Me}}{OCO} \diagup\end{matrix}Co\begin{matrix}OH_2 \\ (NH_3)_3\end{matrix}\right],$$

the nitric acid breaking one of the ol-linkings.

The *nitrate*, $Y(NO_3)_4$, is best prepared by warming a solution of hexammine-μ-amino-diol-dicobalti-nitrate with acetic acid at 70°, and then adding concentrated nitric acid to the cooled solution; bright red leaflets, with acid reaction. The *bromide*, YBr_4, is precipitated from a solution of the nitrate on the addition of 40% hydrobromic acid; red crystals.

[With FRL. MARIE GRIGORIEFF.]—*Hexammine-μ-amino-ol-peroxocobalti-cobalte* salts, YX_3, where $Y = \left[(H_3N)_3\overset{IV}{Co}\begin{matrix}\diagup NH_2 \diagdown \\ OH \longrightarrow \\ \diagdown O_2 \diagup\end{matrix}\overset{III}{Co}(NH_3)_3\right]$. These salts belong to the same series as the ozoimidohexamminedicobalti-salts (Abstr., 1899, ii, 658). The starting point is a black chloride, obtained by the action of silver nitrate on melanochloride (see diaquohexammine-μ-amino-ol-dicobalti-nitrate). The filtrate from the silver chloride,

after the addition of a little ammonium nitrate, is kept for a quarter of an hour. The resulting crystals are collected, and the filtrate mixed with concentrated hydrochloric acid and warmed at 40°. The black chloride then separates; it contains one chlorine atom less and two atoms of oxygen more than melanochloride. To prepare the *bromide*, $YBr_3,2H_2O$, the black chloride is triturated with a concentrated solution of silver nitrate; the filtrate from the silver chloride gives dark green crystals of the bromide on saturation with ammonium bromide. The *chloride*, YCl_3,H_2O, results from the interaction of the bromide and silver chloride, and the *nitrate*, $Y(NO_3)_3,H_2O$, from the double decomposition of the bromide and silver nitrate. The latter forms dark green scales.

The above series of salts also result from the degradation of the octammine-μ-aminoperoxocobalticobalte salts; aqueous solutions of the latter are heated with ammonium chloride, and the reaction mixture saturated with hydrogen chloride, when the hexammine chloride separates. Also, on reduction with potassium iodide and acetic acid they give rise to hexammine-μ-amino-diol-dicobalti-salts.

When an aqueous solution of hexammine-μ-amino-ol-peroxocobalticobalte chloride is warmed with concentrated hydrochloric acid, small, black crystals of s-*dichlorohexammine-μ-aminoperoxocobalticobalte chloride*, YCl_2, where $Y=\left[{}^{Cl}_{(H_3N)_3}Co<^{NH_2}_{-O_2-}>Co^{Cl}_{(NH_3)_3}\right]$, separate. The *nitrate*, $Y(NO_3)_2$, resembles the chloride in appearance, and is obtained from the latter by trituration with concentrated nitric acid. From the corresponding hexammine bromide and hydrobromic acid, small, greenish-black crystals of s-*dibromohexammine-μ-amino-peroxocobalticobalte bromide*, $\left[{}^{Br}_{(H_3N)_3}Co<^{NH_2}_{-O_2-}>Co^{Br}_{(NH_3)_3}\right]Br_2$, are obtained. The action of liquid ammonia on this bromide gives rise to octammine-μ-aminoperoxocobalticobalte bromide, thus proving that the above octammine- and hexammine-peroxo-salts both contain the same nucleus, $\overset{III}{Co}<^{NH_2}_{-O_2-}>\overset{IV}{Co}$.

Reduction of hexammine-μ-aminoperoxo-ol-cobalticobalte bromide with sulphurous acid and addition of concentrated hydrobromic acid to the resulting solution gives greenish-black crystals of tetrabromo-hexammine-μ-aminodicobalti-bromide (q.v.), which with silver nitrate in dilute nitric acid solution gives diaquohexammine-μ-amino-ol-di-cobaltinitrate.

When solutions of octammine-μ-aminoperoxocobalticobalte nitrate are heated with excess of ammonium carbonate instead of ammonium chloride, and the cold reaction mixture then treated with hydrochloric acid, dark olive-green crystals of a chloride are obtained, which is isomeric with the symmetrical dichloro-chloride just described. It is readily soluble in water, however, whereas the symmetrical chloride is sparingly soluble. It contains the nucleus $\overset{III}{Co}<^{NH_2}_{-O_2-}>\overset{II}{Co}$, since liquid ammonia transforms it again into the octammine-μ-aminoperoxo-ol-cobalticobalte salt, and therefore differs from the symmetrical chloride only in the

position of the ammonia molecules. It is as-*dichlorohexammine-μ-aminoperoxocobalticobalte chloride*, YCl_2, where

$$Y = \left[(H_3N)_4Co{<}{}^{NH_2}_{O_2}{>}Co{}^{Cl_2}_{(NH_3)_2}\right].$$

On heating with dilute hydrochloric acid, it is decomposed, with the formation of chloropentamminecobalti-chloride. The *bromide*, YBr_2, is obtained by saturating a solution of the chloride with ammonium bromide; small, glistening, dark brown needles.

Hexammine-μ-acetato-diol-dicobalti salts, YX_3, where

$$Y = \left[(H_3N)_3Co \begin{array}{c} \overset{\displaystyle Me}{\overset{|}{OCO}} \\ OH \\ OH \end{array} Co(NH_3)_3\right]$$

These salts are derived from the hexamminetrioldicobalti-salts, the preparation and constitution of which have been previously described (Abstr., 1908, ii, 43). The *chloride*, $YCl_3,4H_2O$, is prepared by evaporating a concentrated aqueous solution of hexamminetrioldicobalti-chloride on the water-bath with glacial acetic acid; long, red needles; $3H_2O$ are lost at 100—110°. The *bromide*, YBr_3,H_2O, is prepared in a similar way from the corresponding triol bromide; violet-red prisms, which become anhydrous at 110°. It dissolves in saturated hydrochloric acid at 0°, and the blue solution then deposits crystals of trichlorotriammine cobalt, $(H_3N)_3CoCl_3$ (compare Abstr., 1906, ii, 760). The *iodide*, YI_3,H_2O, and the *thiocyanate*, $Y(SCN)_3,H_2O$, are precipitated when a solution of the bromide is saturated with potassium iodide and thiocyanate respectively; red plates and slender, red crystals. The *nitrate*, $Y(NO_3)_3,2HO$, is prepared from the hexamminetriolnitrate by evaporation with glacial acetic acid; shining red, monoclinic prisms, which lose $1H_2O$ at 100—110°. The *bromide dithionate*, $YBr(S_2O_6),H_2O$, forms as a red, crystalline precipitate when sodium dithionate is added to a concentrated solution of diacetatodiaquohexamminedicobalti-bromide.

Diacetatoaquohexammine-ol-dicobalti-bromide,

$$\left[{}^{H_2O}_{(H_3N)_3}Co{<}{}^{\overset{\displaystyle Me}{\overset{|}{OCO}}}_{OH}{>}Co{}^{OCOMe}_{(NH_3)_3}\right]Br,$$

is obtained in red needles when a saturated solution of hexammine-triol-dicobalti-bromide is mixed with half its volume of glacial acetic acid and the solution evaporated to half its original volume on the water-bath. It is very unstable in aqueous solution, salts of the metals always giving precipitates of the hexammine-μ-acetato-diol-dicobalti-series.

[With ADOLF GRÜN and EMIL BINDSCHEDLER].—*Hexammine-diol-μ-nitrodicobalti*-salts, YX_3, where $Y = \left[(H_3N)_3Co \begin{array}{c} OH \\ OH \\ NO_2 \end{array} Co(NH_3)_3\right]$.

These salts are formed by the action of nitrous acid on the hexamminetrioldicobalti-salts in acetic acid-aqueous solution. They are deep orange in colour, and the nitro-group is very firmly combined.

On warming with hydrochloric or hydrobromic acids, an ol-linking is broken, two halogen atoms entering into the complex radicle.

The *chloride*, YCl_3,H_2O, is formed from the hexamminetriol chloride in the way indicated, and precipitated from solution by the addition of concentrated hydrochloric acid; felted, orange-red needles. The *bromide*, YBr_3,H_2O, forms orange-red, felted leaflets. The *nitrate*, $Y(NO_3)_3,H_2O$, is precipitated in orange-red, rhombic plates on adding nitric acid to a solution of the chloride. Sodium sulphate precipitates the *sulphate*, $Y_2(SO_4)_3$, in orange-red, rhombic, prismatic crystals.

[With EMIL BINDSCHEDLER and E. WELTI].—*Dichlorohexammine-μ-nitro-ol-dicobalti*-salts, YX_2, where

$$Y=\left[{}^{Cl}_{(H_3N)_3}Co<\begin{matrix}OH\\NO_2\end{matrix}>Co^{Cl}_{(NH_3)_3}\right].$$

The *chloride*, YCl_2 is obtained as a dark violet, crystalline compound when hexammine-μ-nitro-diol-dicobalti-chloride is heated on the water-bath with concentrated hydrochloric acid. It is sparingly soluble in cold water, and the violet solution in warm water changes to a red colour, from which the original hexammine-μ-nitrodiol chloride is precipitated by hydrochloric acid. The *nitrate*, $Y(NO_3)_2$, may be obtained from the chloride either by the action of concentrated nitric acid or sodium nitrate; dark violet crystals. With sodium sulphate, the *sulphate*, YSO_4,H_2O, is produced, and with sodium dithionate, violet crystals of the *dithionate*, YS_2O_6.

[With E. WELTI.]—*Dibromohexammine-μ-nitro-ol-dicobalti*-salts, YX_2, where $Y=\left[{}^{Br}_{(H_3N)_3}Co<\begin{matrix}OH\\NO_2\end{matrix}>Co^{Br}_{(NH_3)_3}\right]$, are obtained from the hexammine-μ-nitrodiol salts in a similar manner to the dichloro-salts. The *bromide*, YBr_2, is a greyish-black, crystalline powder, as also are the *nitrate*, $Y(NO_3)_2$, and the *dithionate*, YS_2O_6.

Hexammine-μ-ol-dinitrodicobalti-chloride,

$$\left[(H_3N)_3Co\begin{matrix}OH\\NO_2\\NO_2\end{matrix}Co(NH_3)_3\right]Cl_3+\tfrac{1}{2}H_2O,$$

is formed from dichlorohexammine-μ-nitro-ol-dicobalti-chloride by the action of nitrous acid in acetic acid solution. It is precipitated from solution in reddish-orange needles by the addition of nitric acid. Both the ol- and the nitro-linkings are very stable, since the salt can be recrystallised from hydrochloric acid.

Hydroxoaquohexammine-μ-peroxo-ol-cobalticobalte salts, YX_3, where $Y=\left[{}^{HO}_{(H_3N)_3}Co<\begin{matrix}O_2\\OH\end{matrix}>Co^{OH_2}_{(NH_3)_3}\right]$. When melanochloride is prepared by the exposure of ammoniacal cobalt chloride solutions to the air at temperatures below 5°, and then worked up with silver nitrate, it yields a brownish-black nitrate in addition to the salts of the hexammine-μ-aminoperoxo-ol-cobalticobalte series. From this brownish-black nitrate, the pure *sulphate*, $Y(SO_4)_3$, may be obtained by a complicated process; shining brown crystals. On heating with concentrated sulphuric acid, it is decomposed with evolution of oxygen and nitrogen, the volumes of these gases obtained showing that the compound contains a peroxo-group and tervalent and quadrivalent cobalt. The

double salt with ammonium sulphate, $Y(SO_4)_2NH_4,H_2O$, is precipitated when glacial acetic acid is added to a solution of the nitrate saturated with ammonium sulphate; black crystals. The following salts are prepared by double decomposition of the sulphate with various ammonium salts. The *chloride*, YCl_3, brown needles; *bromide*, YBr_3,H_2O, greenish-brown needles; *nitrate*, $Y(NO_3)_3$, blackish-brown leaflets. When a cold solution of the nitrate in water containing acetic acid is mixed with concentrated hydrochloric acid, small, greyish-black crystals of *trichlorohydroxohexammine-μ-peroxocobalticobalte chloride*, YCl, where $Y = \left[\overset{Cl}{\underset{(H_3N)_3}{HOCo}}\cdot O_2\cdot Co{}^{Cl_2}_{(NH_3)_3}\right]$, are obtained. The *nitrate*, YNO_3, is obtained from the chloride by precipitation with concentrated nitric acid. By the action of liquid ammonia on the chloride, hexammine- and chloropentammine-cobalti-chloride are obtained, proving that the two cobalt atoms of the original substance cannot be joined by a μ-amino-linking, since such a linking is not severed by the action of ammonia.

When hydroxoaquohexammine-μ-peroxo-ol-cobalticobalte sulphate is reduced with acetic acid and sodium iodide, and the liberated iodine destroyed with sodium thiosulphate, pale red crystals are obtained, which on treatment with ammonium bromide give bluish-red plates of hexammine-μ-acetato-diol-dicobalti-bromide (q.v.). The arrangement of the ammonia molecules in the two series of salts is thus proved to be the same.

Hexamminehexoltricobalti-salts, YX_3, where

$$Y = \left[(H_3N)_3Co\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}Co\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}Co(NH_3)_3\right]$$

In the preparation of hexamminetrioldicobalti-sulphate from chlorodiaquotriamminecobalti-sulphate (Abstr., 1908, ii, 43), a reddish-brown mother liquor is obtained, which, when strongly cooled, gives a green precipitate on the addition of concentrated hydrochloric acid. The green precipitate is dissolved in water, acidified with acetic acid, and precipitated as the impure sulphate by the addition of sodium sulphate. From the sulphate, by treatment with ammonium chloride, greenish-brown crystals of pure *hexamminehexoltricobalti-chloride*, $YCl_3,3H_2O$, can be obtained. The *bromide*, YBr_3, is obtained from the chloride by the action of ammonium bromide, and the *dithionate*, $Y_2(S_2O_6)_3,2H_2O$, by the action of sodium dithionate; brown crystals in both cases.

When these salts are decomposed by hydrochloric acid, the products are dichloroaquotriamminecobalt chloride, $\left[Cl_2Co{}^{OH_2}_{(NH_3)_3}\right]Cl$, cobaltous chloride, and chlorine. The formation of triammine salts shows that the six ammonia molecules are divided equally between two cobalt atoms, and the chlorine is a result of the reduction of the third cobalt atom from tervalent to bivalent cobalt. There are no μ-amino-linkings, and hence the constitution given above.

When solutions of hexamminehexoltricobalti-salts are precipitated with concentrated hydrochloric acid in the cold, one of the ol-linkings is destroyed, and green crystals of *diaquohexamminepentoltricobalti-*

chloride, $\left[\begin{matrix}H_2O\\(H_3N)_3\end{matrix}Co\left\langle\begin{matrix}OH\\H_2O\\OH\end{matrix}\right\rangle Co\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right\rangle Co(NH_3)_3\right]Cl_4$, are obtained. It is not yet certain whether all the chlorine atoms are ionic in character.

For other complex metal ammonias, see Abstr., 1907, i, 482, 1012.

T. S. P.

Tungstic Acid Hydrosol. ALFRED LOTTERMOSER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1910, II, 70—71).—When a not too dilute solution of hydrochloric acid is added to a concentrated solution of sodium tungstate, a voluminous, gelatinous, white precipitate is formed. More dilute solutions remain clear at first, and afterwards slowly deposit the white precipitate in a more voluminous form. If the precipitate formed from very dilute solutions is repeatedly decanted with distilled water, a clear hydrosol may be obtained, which, however, is unstable, as it gradually becomes cloudy, and changes to a hydrosol which is yellow in reflected light. When more concentrated solutions are used, the voluminous, white precipitate gradually decreases in bulk, at the same time turning yellow; finally, the same yellow hydrosol is obtained as previously. If this yellow hydrosol is shaken, a silky lustre is noticeable in reflected light, although it appears clear in transmitted light; it is a suspension of relatively large particles, and gradually clears on keeping.

The above phenomena illustrate the gradual and continuous change from a solution, or molecular-disperse system, through a hydrosol, which is clear in both transmitted and reflected light, to a jelly. The jelly is not stable, however, and undergoes an irreversible transformation into a suspension. T. S. P.

Mutual Influence of Colloidal Tungstic and Molybdic Acids. LOTHAR WÖHLER and W. ENGELS (*Koll. Chem. Beihefte*, 1910, 1, 454—476).—Experiments are described which show that the precipitation which occurs when solutions of molybdates are acidified is due to the presence of tungstates. The readiness with which precipitation takes place is dependent on the proportion of tungstic acid present, and when this is present in very small amount, the temperature may be raised to nearly 100° before a precipitate is obtained. The precipitation is primarily due to the tungstic acid in the solution, and when this separates out, molybdic acid is simultaneously removed from the solution. Experiments have been made to determine the dependence of the composition of the precipitate on that of the solution. It is found that the quantitative extraction of tungstic acid in presence of large quantities of molybdic acid can be effected by precipitation with hydrogen sulphide in tartaric acid solution.

Dialysis experiments and ultramicroscopic observations indicate that molybdic acid can be obtained in colloidal form, and that colloidal molybdic acid is present in solutions of the molybdates. The precipitation which occurs on acidification of impure molybdate solutions is due to the mutual influence of the colloidal forms of tungstic and

molybdic acids. In consequence of this mutual influence, commercial tungstic acid always contains appreciable quantities of molybdic acid.

H. M. D.

Zirconium Sulphates. III. The 4 : 3 Basic Zirconium Sulphate and its Hydrates. OTTO HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1910, **67**, 369—375).—The salt $4ZrO_2,3SO_3$, containing water of crystallisation (Abstr., 1905, ii, 531), is so well defined as to be suitable for atomic weight determinations. Its properties have therefore been further studied. The ratio $ZrO_2 : SO_3$ is very constant. When dried over dilute sulphuric acid, D 1·256, the salt contains $15H_2O$. It forms monoclinic, microscopic needles, D 2·50, and is very stable towards dilute acids. The loss of water when dried over sulphuric acid of increasing concentration is continuous until the hydrate $4ZrO_2,3SO_3,7H_2O$ is reached, and the process of dehydration is not reversible. Careful heating for a long time at 105—115° yields a salt containing $5H_2O$, and the anhydrous salt, D 4·1, is obtained at 300°. The pentahydrate may be regarded as $Zr_4(SO_3)_3(OH)_{10}$, and as the parent substance of the higher hydrates. An attempt to replace the hydroxyl by chlorine gave only indefinite products. C. H. D.

Compounds of Thorium Chloride with Ammonia. ÉDOUARD CHAUVENET (*Compt. rend.*, 1910, **151**, 387—389).—The composition of the compounds prepared is given in tabular form, together with their heat of dissolution in hydrochloric acid, the approximate temperature of formation and decomposition, and in each case the heat of fixation of $1NH_3$ on the preceding member of the series. The compounds mentioned are of the type $ThCl_4,nNH_3$, and may be classified into three groups: (1) $n = 4, 6, 7, 12$, and 18. These are obtained by treating thorium choloride with liquid ammonia, and allowing the product to remain at different temperatures. They are decomposed by water, and in a vacuum lose ammonia, forming the compound $ThCl_4,4NH_3$. (2) $n = 4, 6$, or 7. The members of this group are prepared by leaving the chloride in contact with gaseous ammonia. They remain unaltered when placed in a vacuum or treated with water. (3) $n = 6, 7, 12$, or 18. These compounds are obtained by the addition of liquid ammonia to members of the second group; the first two terms of this group are identical with the last two of the second.

The compound $ThCl_4,4NH_3$ of the second group, is the only one in the whole series stable above 120°. At 250—300°, however, this loses hydrogen chloride and forms thorium tetramide, whilst at a red heat the amide $Th(NH_2)_2$ is obtained. W. O. W.

The Equilibrium Diagram of the Gold-Magnesium Alloys. G. G. URAZOFF and RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1910, **67**, 442—447. Compare Vogel, Abstr., 1909, ii, 896; Urazoff, this vol., ii, 43).—The differences between the results previously obtained by the two authors are discussed and explained. The existence of Urazoff's compound, Au_2Mg_5, is confirmed, as is that of Vogel's transformation to $AuMg_2$ and $AuMg_3$ on cooling to 716°. The curve representing the

change in concentration of the solid solution Au–AuMg on cooling has the form given it by Vogel; in the remaining curves Urazoff's data are to be preferred. C. H. D.

Mineralogical Chemistry.

Ludwigite from Montana. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], **30**, 146—150).—Ludwigite, a mineral hitherto known only from Morawitza, in Hungary, has been found at Philipsburg, Montana, as small spherulites, with a radiated structure and a dark green or nearly black colour, in metamorphosed limestone with large bodies of magnetite. Under the microscope the fibres give straight extinction and are strongly pleochroic (sea-green for vibrations parallel to their length, and chestnut-brown perpendicular to this). Embedded in the material is an olivine (perhaps forsterite), a carbonate (perhaps magnesite or chalybite), and a colourless fibrous mineral. The material analysed (anal. I) was, therefore, not quite pure; deducting forsterite, etc., the composition is as given under II, and neglecting water and alumina, the formula becomes $4(Fe,Mg)O,Fe_2O_3,B_2O_3$.

	B_2O_3.	MgO.	FeO.	Fe_2O_3.	SiO_2.	Al_2O_3.	H_2O (105°).	H_2O (>105°).	CO_2.	Total.
I.	13·48	39·04	5·79	29·73	8·85	1·81	0·97	0·90	0·36	100·93
II.	16·94	33·78	7·27	37·37	—	2·27	1·24	1·13	—	100·00
III.*	[17·02]	28·88	15·84	35·67	—	—	0·51	0·82	0·90	100·00

* Also insoluble, 0·36.

A new analysis of the Hungarian ludwigite is given under III, agreeing with the formula previously given for the mineral, namely, $3MgO,FeO,Fe_2O_3,Br_2O_3$. The Montana ludwigite differs from this in having a portion of the ferrous oxide isomorphously replaced by magnesia. L. J. S.

The Play of Colour of Alexandrite. OTTO HAUSER (*Zeitsch. angew. Chem.*, 1910, **23**, 1464—1465).—Alexandrite, a variety of chrysoberyl, is dark green in daylight, but cherry-red in artificial light. This play of colour is independent of the crystallographic form of alexandrite, and is due to a slight admixture of chromic oxide, which is present partly in colloidal solid solution, and partly as an isomorphous mixture.

Solutions of chromium sulphate which have been gently boiled, of chromium thiocyanate, and alkaline chromite solutions show the same phenomenon, being green in daylight and red in artificial light. Such solutions contain chromium oxide partly in colloidal, and partly in molecular solution. T. S. P.

Effect of the Presence of Alkalis in Beryl on its Optical Characters. WILLIAM E. FORD (*Amer. J. Sci.*, 1910, [iv], **30**, 128—130).—The following analyses are of pink beryls from: (I) Mesa

Grande, San Diego Co., California; (II) Pala, San Diego Co., California; (III) Madagascar:

	SiO_2.	Al_2O_3.	MnO.	GlO.	Cs_2O.	K_2O.	Na_2O.	Li_2O.	Ignition.	Total.
I.	64·98	17·86	—	13·42	—	0·18	0 84	0·46	2·16	99 90
II.	n. d.	n. d.	—	n. d.	0·57	0·28	1·59	1·33	n d.	—
III.	62·79	17·73	trace	11·43	1·70	—	1·60	1·68	2·65	99·58

The refractive indices of this material, and also of beryls rich in alkalis from Willimantic, Connecticut, and from Hebron, Maine, analysed by Penfield (1888) and by Wells (1892) respectively are:

Locality.	ω.	ϵ.	$\omega - \epsilon$.	Total alkalis.	Sp gr.
Mesa Grande...	1 58157	n. d.	—	1·48	2·714
Willimantic ...	1·58455	1·57835	0·00620	1·15	2·73
Pala	1·59239	1·58488	0·00751	3·77	2·785
Madagascar ...	1 59500	1·58691 *	0·00809 *	4·98	2·79
Hebron	1·59824	1·59014	0·00810	6·33 †	2·80

* Approximate. † Namely, Cs_2O, 3·60; Na_2O, 1·13; Li_2O, 1·60.

It is thus seen that with a replacement of glucina by alkalis there is (with the increased molecular weight) an increase in the values of the refractive indices, birefringence, and specific gravity. L. J. S.

Chemical and Optical Study of a Labradorite. WILLIAM E. FORD and W. M. BRADLEY (*Amer. J. Sci.*, 1910, [iv], **30**, 151—153).—Perfectly clear and almost colourless (the larger pieces showing a faint tinge of yellow), water-worn pebbles of labradorite from the Altai Mountains in Mexico (close to the New Mexico boundary) gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Fe_2O_3.	Ignition.	Total.	Sp gr.
51·24	30·84	13·59	3·76	0·17	0·73	0 24	100·57	2·718

This corresponds with albite : anorthite = 1 : 1·918. The iron is due to the enclosure of minute scales of hæmatite arranged parallel to the cleavages; these enclosures produce a metallic reflexion, as in the sunstone from Norway. The angle between the cleavages is $cb = 85°49'$; the cleavage $b(010)$ is imperfect and difficult to obtain. The angles of optical extinction are: on $b(010)$, $-24°37'$; on $c(001)$, $-12°13'$.

L. J. S.

Axinite from California. WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1910, **48**, 148—157).—Opaque, smoke-grey crystals of axinite, measuring up to 5 cm. across, are found loose in decomposed granite at Moosa Cañon, near Bonsall, in San Diego Co.; the associated minerals are quartz, epidote, and laumontite. Analysis I agrees with the formula:

$$8SiO_2,2Al_2O_3,2(Fe,Mn,Mg)O,4CaO,H_2O,B_2O_3.$$

Several analyses previously published are tabulated and found to agree closely with this formula, in which the atomic amount of calcium is constant, whilst the manganous oxide and ferrous oxide replace each other isomorphously. For the end members of the series, the names ferroaxinite, $Al_2BHCa_2FeSi_4O_{16}$, and manganoaxinite,

$$Al_2BHCa_2,MnSi_4O_{16},$$

are proposed. It is pointed out that the sp. gr. (3 268 to 3·358) of axinite increases progressively with the percentage of manganese.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	H_2O.	B_2O_3.	Total.
I.	42·61	17·43	0·38	7·53	4·10	0·44	19·74	1·56	6 04	99·83
II.	42·79	16·38	—	4·22	8·76	0·09	19·21	1·85	[6·70]	100·00

Small, transparent crystals of axinite from the Consumes copper mine in Amador Co. are associated with epidote and quartz. Several new crystal-forms are noted. Analysis II, made on a small amount of not quite pure material, also agrees with the above formula.

L. J. S.

Physiological Chemistry.

Quantitative Investigations on the Absorption of Benzene from the Air by Men and Animals. KARL B. LEHMANN, KARL GUNDERMANN, OTTMAR STÖHR, and R. KLEINER (*Arch. Hygiene*, 1910, **72**, 307—326).—The benzene was inhaled mixed with air, and exhaled over cooled flasks containing liquid paraffin. The latter were afterwards warmed to 100° in a current of air, which was then lead through absorbers containing a mixture of nitric and sulphuric acids, and the benzene thereby converted into the dinitro-derivative, in which form it was weighed. In the human experiments, about 80% was absorbed. Experiments were also carried out with rabbits in various ways. In the majority, the tracheotomised animals breathed through a valve from a chamber in which benzene vapour was pressed in by means of air, and mixed with other air sucked into the chamber by a pump. It was also expired through cooled paraffin absorption flasks. The absorption in the first half-hours was about 37—54·5% of the benzene inspired. There is in most animals a fall in the percentage absorbed during this period, but the amount taken up durihg the next three or four hours remains constant in most cases. Individual animals showed, however, considerable variations, just as Nencki showed that there are considerable variations in the amount of benzene converted into phenol in different animals. These, perhaps, bear some relationship to the benzene absorbed from inspired air. S. B. S.

Experiments Made on Mont Blanc, in 1909, on Variations in Glycæmia and Hæmatic Glycolysis at a Very High Altitude. RAOUL BAYEUX (*Compt. rend.*, 1910, **151**, 449—451).—The experiments were carried out on rabbits at Chamonix, and at an altitude of 4350 metres on Mont Blanc, under a pressure of 450 mm. In each animal blood was withdrawn from the heart, defibrinated, and the sugar estimated immediately in one part, and in the other after glycolysis had been allowed to proceed for an hour at 39°. The conclusions drawn are that the amount of sugar and the speed of glycolysis are both diminished at high altitudes, but that the variations are independent

of alterations in the animal temperature. Death supervenes when glycolysis is diminished to the extent of 60%. W. O. W.

Origin and Importance of the Amylolytic Blood Ferment. KURT MOECKEL and FRANZ ROST (*Zeitsch. physiol. Chem.*, 1910, **67**, 433—485).—The amount of amylase in the blood of different species of animals varies considerably, and corresponds with the digestive power. The amounts present in the urine do not show great variations.

The amount of ferment in the blood may be increased by cold, and tends to increase under the influence of hunger. Animal diastase introduced per os, per rectum, and subcutaneously does not increase the blood diastase.

Pilocarpin causes an increase both of amylase and of maltase in the blood-serum. Phloridzin and adrenaline have no effect. Strychnine poisoning generally results in an increase of diastase in the blood.

Human diabetes is usually coincident with diminished amounts of diastase.

The diastase is partly eliminated in the urine, and a part becomes inactive in the body. Impermeability of the kidneys generally gives rise to a not very considerable increase of diastase in the body.

N. H. J. M.

Question as to the Identity of Pepsin and Chymosin. W. SAWITSCH (*Zeitsch. physiol. Chem.*, 1910, **68**, 12—25. Compare Bang, Abstr., 1900, ii, 356; Hammarsten, *ibid.*, 1908, i, 588).—In Hammarsten's method for isolating pepsin from chymosin. the latter is not destroyed, but the properties of the ferment are so altered that samples usually show negative coagulating properties.

Calves' rennin when kept in a thermostat alters in properties and then resembles Bang's parachymosin.

Although ferment solutions from different kinds of animals have different properties, it does not follow that the pepsins of different animals are not identical. The differences in properties are mainly of degree of resistance or reactivity, and it is shown that a ferment solution from a single animal can also vary considerably in properties according to the conditions of the experiment, and the non-reactivity of the solution does not necessarily mean the absence of the ferment; it may be due to the conversion of the ferment into its inactive form. It is possible that the difference in behaviour of different solutions is due to the presence of compounds of pepsin with various substances.

J. J. S.

Comparative Investigations on the Activities of Pepsin and Chymosin of Dogs and Calves. OLAF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1910, **68**, 119—159).—Infusions of dogs' and calves' stomachs have been examined, and it is shown that the peptic and coagulating effects are quite different. Both extracts were made to contain 0·2% hydrochloric acid. Although the infusion from dogs contained twice as much pepsin as that from calves, it was found that at dilutions 1/10—1/80 the dogs' extract was incapable of curdling cow's milk, whereas extracts of the same concentration from calves

readily produced coagulation. In the case of the canine extract, the curdling did not follow the ordinary time law. The difference in behaviour was not due to the fact that the extract from dogs contained inhibiting substances, as when added to calves' infusion it produced much the same effects as diluting the latter extract with 0·2% hydrochloric acid.

An increase in the acidity of the infusion had a more marked effect on the dogs' enzyme than on the calves, and, by the addition of acid, it was found possible to obtain solutions of the two infusions with equal curdling powers, but the peptonising powers of two such extracts were as 1 : 50 (calves : dogs).

Calcium chloride also had a greater accelerating influence than acid, and in this case also the effect was more marked in the case of the infusion from dogs' stomachs, but it was not found possible to prepare solutions of the two infusions identical as regards both peptonising and curdling properties.

The addition of either acid or calcium chloride to dogs' infusion restores the ordinary time law.

It is pointed out that the addition of calcium chloride to milk, as in Migay and Sawitsch's experiments (this vol., ii, 140), increases the acidity of the milk (compare Dam, Abstr., 1909, i, 278). The results obtained support the view that peptonising and coagulating effects are due to enzymes (dualistic view).

The view that the difference is entirely due to the fact that cow's milk contains substances which inhibit the action of dogs' enzyme does not appear tenable, as experiments have been made with casein solutions in place of milk, and in these experiments complete parallelism between the two effects could not be obtained. Arguments against the view that the infusions themselves contain substances with inhibiting properties are also brought forward.

J. J. S.

Utilisation in the Animal Organism of Protein Cleavage Products. EMIL ABDERHALDEN and PETER RONA (*Zeitsch. physiol. Chem.*, 1910, **67**, 405—411. Compare Abderhalden and Prym, Abstr., 1907, ii, 897).—It is shown that the preparations employed in experiments with protein cleavage products contained practically only amino-acids. By the combined digestion of proteins, especially meat, with pepsin and hydrochloric acid, trypsin, and erepsin, complete hydrolysis is readily obtained in three or four weeks, and probably less.

N. H. J. M.

Digestion of Cellulose. II. The Ingestion of Cellulose by the Dog. HEINRICH VON HOESSLIN (*Zeitsch. Biol.*, 1910, **54**, 395—398. Compare this vol., ii, 626).—The author criticises the technique of Lohrisch and Simon, and, quoting his own and Scheuvert's experiments, considers that there is no evidence of the absorption of pure white cabbage cellulose in the intestine of the dog.

G. S. W.

The Mechanism of the Influence of the Hardness of Water on Bodily Development. RAGNAR BERG (*Biochem. Zeitsch.*, 1910, **27**, 204—222).—It has been shown previously that bodily develop-

ment is impeded by a want of calcium salts, and the same cause has a deleterious influence on the excretions and secretions, and that these factors bear accordingly a direct relationship to the hardness of water. The author has carried out experiments and collected statistics to find in what manner the hardness of water acts. He finds that there is no direct relationship between the mineral contents of vegetables and the hardness of water in the neighbourhoods in which they are grown. There is, however, a direct relationship between the contents of cooked vegetables and the hardness of water in which they are cooked, those vegetables which are cooked in hard water having a greater calcium content after cooking than those cooked in soft water. These results were derived from experiments both on natural water and water hardened by different calcium salts. The author also gives statistics showing generally that in neighbourhoods with hard water, the children are suckled by their mothers for longer periods than in neighbourhoods with soft water. The mineral contents of milk exerted no influence on the difference of digestibility of boiled and unboiled milk. The calcium salts of digested milk are soluble both in acid and alkaline liquids, and dialysable. The calcium that is rendered insoluble by rennet is apparently not present as inorganic salt.

S. B. S.

The Inhibition by Potassium Cyanide of the Deleterious Action of Salt Solutions on the Fertilised Egg. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, **27**, 304—311).—It has been shown that if the fertilised egg of sea-urchins be placed in solutions of the chlorides of the alkali metals isotonic with sea-water, and be then returned to sea-water, they undergo cytolysis. It is now shown that this deleterious action can be inhibited if small quantities of potassium cyanide be added to the salt solutions. To explain the result, it is assumed that the hydrolytically dissociated part of the salt enters into action in the cell, the hydroxides of the alkali metals forming salts with the acid constituents of the cell, which undergo oxidation. The oxidation products act cytolytically, but are precipitated by the salts of dyad metals. Potassium cyanide acts by inhibiting this oxidation.

S. B. S.

Action of Some Organic Salts of the Alkalis on Muscle, Blood Corpuscles, Protein, and Lecithin. RUDOLF HÖBER (*Pflüger's Archiv*, 1910, **134**, 311—336. Compare this vol., ii, 330, and Abstr., 1909, ii, 251).—Continuing his studies on the parallelism between the physiological and the physico-chemical properties of neutral salt solutions, the author has investigated the action of solutions of the alkali salts of a number of organic acids on the resting current in muscle, the diminution of muscular excitability, the coagulation of protein substances by heat, the precipitation of proteins, and the precipitation of lecithin. He finds that in all these actions the organic cations fall into approximately the same series, namely, tartrate, sulphate (formate, acetate, propionate, butyrate, valerate), chloride, iodide. The effects of those of which the names are enclosed in brackets are nearly equal. The sodium and lithium

salts of salicylic and benzoic acids exhibit, however, no such parallelism, and their actions are not reversible.

The hæmolytic effect of the various salts is the same for blood corpuscles of different animals, and runs fairly parallel to their other actions already mentioned. The typical hæmolytic substances, such as saponin and solanin, generate in muscle an irreversible resting current in the normal direction, and diminish to a corresponding degree its excitability. R. V. S.

Extractives of Muscles. XI. Nitrogenous Extractive Substances of Veal and Beef. WLADISLAW SKWARZOFF (*Zeitsch. physiol. Chem.*, 1910, **68**, 26—39. Compare Krimberg, Abstr., 1908, ii, 609).—Aqueous extracts of veal yielded carnosine (0·176), methylguanidine (0·022), and carnitine (0·019%). N. H. J. M.

Occurrence of Choline in Testicles of Oxen. G. TOTANI (*Zeitsch. physiol. Chem.*, 1910, **68**, 86—87).—The author finds that choline is a normal constituent of oxen testicles (compare Dixon, Abstr., 1901, ii, 259). J. J. S.

The Bile of Polar Animals. IV. The Bile of Seals. OLAF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1910, **68**, 109—118. Compare Abstr., 1909, ii, 819).—The bile of the following species has been examined: *Phoca barbata*, *P. groenlandica*, *P. foetida*, *Cystophora cristata*. In each case the bile contained much taurocholate and but little glycocholate, and hence the aqueous solutions were not precipitated by lead acetate, copper sulphate, alum, calcium chloride, or barium chloride. Ferric chloride gave precipitates containing appreciable amounts of colouring matter together with tannic acids. Most of the biles contained only small amounts of phosphatides. The numbers varied from traces in the case of *P. barbata* to 14% in the case of *Cystophora cristata*.

Bilirubin and urobilin could not be detected in the bile of *C. cristata*, and urobilin was absent from the gall of *P. groenlandica*, but was present in appreciable quantity in that of *P. barbata*.

A glycocholic acid, not identical with the ordinary acid, small amounts of α-phocaetaurocholic acid, appreciable amounts of β-phocaetaurocholic acid, and an acid, probably taurocholeic acid, were isolated from the bile of *P. barbata*. Of the bile acids present in *P. groenlandica*, 44·52% consisted of α-phocaetaurocholic acid; appreciable amounts of the β-acid were also found.

Taurocholic acid and the α- and β-phocaetaurocholic acids were also detected in the gall of *P. foetida*.

Cystophora cristata gave a glycocholic acid, probably glycocholeic acid, small amounts of α- and β-phocoetaurocholic acids, and much taurocholic acid. J. J. S.

The Neutral Sulphur of Urine and its Relationship to the Diazo-reaction and the Elimination of Proteic Acids. MORIZ WEISS (*Biochem. Zeitsch.*, 1910, **27**, 175—203).—The diazoreaction of Ehrlich is according to more recent researches due to

the hydroxyproteic acids which contain sulphur. The author has accordingly investigated the quantitative relationship between the neutral sulphur and the diazo-reaction, and also the amount of hydroxyproteic acid excreted. He gives a summary of the results of other observers on the elimination of neutral sulphur, and also his own determinations. He concludes therefrom that the groups yielding neutral sulphur are derived partly from the ingested food and partly from the proteins of the organism (exogenous and endogenous portions). The latter yield larger quantities of neutral sulphur, and the latter is increased under conditions, such as the influence of toxic substances, which cause a break down of the body proteins. In tuberculosis of the lungs, the neutral sulphur excreted increases both absolutely and relatively, and there is also a corresponding increase in the Ehrlich diazo-reaction. In carcinoma, the largest quantities of neutral sulphur were found. It appears, therefore, as if the neutral sulphur may be regarded as a measure of the amount of hydroxyproteic acids excreted.

S. B. S.

The Excretion of Ethereal Sulphates and Glycuronic Acids after Administration of Aromatic Compounds. FELIX STERN (*Zeitsch. physiol. Chem.*, 1910, **68**, 52—68).—Experiments have shown that after the administration of aromatic substances there is a considerable increase in the amounts of glycuronic acid excreted, even when the preformed sulphuric acid is not completely exhausted. The increase in the ethereal sulphates takes place more promptly than an increase in the glycuronic acid, especially when indole and cresol are used.

The amount of ethereal sulphates gives a sure measure for the excretion of aromatic compounds when only small amounts are present. With large quantities of aromatic substances, account must be taken of both ethereal sulphates and glycuronic acid (compare P. Mayer, Abstr., 1902, ii, 520, 616).

J. J. S.

Behaviour of Benzoic Acid in the Organism of Fowls in Presence of Glycine. J. YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1910, **68**, 79—82).—The organism of fowls is not able to effect the synthesis of hippuric acid from benzoic acid and glycine fed simultaneously.

N. H. J. M.

Behaviour of Phenylacetic Acid in Fowls. G. TOTANI (*Zeitsch. physiol. Chem.*, 1910, **68**, 75—78).—When consumed by fowls, phenylacetic acid combines with ornithine with the production of phenylaceto-ornithuric acid, which probably has the constitution $CH_2Ph\cdot CO\cdot NH\cdot[CH_2]_3\cdot CH(NH\cdot CO\cdot CH_2Ph)\cdot CO_2H$.

N. H. J. M.

Physiological Degradation of Acids and the Synthesis of an Amino-acid in Animals. FRANZ KNOOP (*Zeitsch. physiol. Chem.*, 1910, **67**, 489—502)—α-Amino-acids, after parting with the amino- and carboxyl groups, are broken down in a manner similar to the next lower fatty acids. They may be acetylated in the bodies of animals.

α-Ketonic acids may take up nitrogen in organic combination in the bodies of animals with production of optically active α-amino-acids. α-Hydroxy-acids may also be converted into α-amino-acids.

N. H. J. M.

Physiological Actions of an Ergot Base and of β-Iminazolyl-ethylamine [β-Amino-4-ethylglyoxaline]. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1910, **54**, 387—394).—A physiological comparison is made of β-amino-4-ethylglyoxaline and a base from ergot which exerts a specific action on the cat's uterus. The conclusion is drawn that they are not identical (compare, however, Barger and Dale, this vol., ii, 736).

G. S. W.

Inurement to Adrenaline. LEO POLLAK (*Zeitsch. physiol. Chem.*, 1910, **68**, 69—74).—Experiments with rabbits showed that injection of *r*-adrenaline during a prolonged preliminary period had as little protective action on the effect of *l*-adrenaline as the employment of *l*-adrenaline itself.

N. H. J. M.

Behaviour of Pyridine in the Organisms of Goats and Pigs. G. TOTANI and Z. HOSHIAI (*Zeitsch. physiol. Chem.*, 1910, **68**, 83—84).—Experiments in which two goats and a pig, fed on an exclusively vegetable diet, received different amounts of pyridine, injected subcutaneously, showed that methylpyridine is produced and is eliminated in the urine.

N. H. J. M.

[Physiological] Action of Cholin. FRANZ MÜLLER (*Pflüger's Archiv*, 1910, **134**, 289—310. Compare Abderhalden and Müller, this vol., ii, 725).—The fall of blood-pressure produced by choline is partly due to its action on the heart and partly to dilatation of the blood vessels. Choline also produces vasoconstriction, however, and this alone is observed on transfusion of the vascular system subsequently to the action of atropine. Choline acts on intestinal muscle both when the plexus has been removed and when it has not. Experiments with isolated muscle from the intestine, uterus, and iris show a great analogy to the action of physostigmine. The occurrence of a rise of pressure after atropine plus choline is probably due to paralysis of the dilatatory elements of the walls of the vessels by the atropine.

R. V. S.

The Influence of Quinine on Experimental Trypanosome Infection. JULIUS MORGENROTH and L. HALBERSTAEDTER (*Sitzungsber. K. Akad. Berlin*, 1910, 732—748).—The propylactic action of quinine and various quinine derivatives, such as cinchonine, euquinine, hydrochloroquinine, and hydrochloro*iso*quinine was investigated. Under certain conditions a marked propylactic action could be ascertained, and was manifested by the longer duration of the life of mice after infection with trypanosome strains. After peritoneal injection, even when the dose of alkaloid was almost toxic to the animal, no protection was obtained. After subcutaneous injection, the protection was more marked, and it was more marked still when the drug was taken *per os*.

The authors discuss the theory of these results, and regard the total action of the drug on the host ("organoergy") as the product of two factors, "organotropy" × sensitiveness.

In a similar way the action on the parasite ("parasitergy") is also a product of the factors, "parasitotropy" × sensitiveness. When "organoergy" is greater than "parasitergy" the drug will injure the host without killing the parasite. In the reverse case, the drug can exert action on the parasite. S. B. S.

Negative Ferric Hydroxide. III. Arsenic and Iron. HERMANN W. FISCHER and ERICH KUZNITZSKY (*Biochem. Zeitsch.*, 1910, 27, 311—325. Compare this vol., ii, 856).—Numerous experiments on animals, carried out chiefly with rabbits, were undertaken with a view to determine the action of colloidal ferric hydroxide as an antidote to arsenic poisoning. The positive ferric hydroxide had a slight antidotal action, and the negative colloid a somewhat stronger action. The conclusion was drawn, however, that a satisfactory antidote in the form of a colloidal ferric hydroxide could not be obtained. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Abiotic Action of Ultra-violet Rays of Chemical Origin. EUGÈNE TASSILLY and R. CAMBIER (*Compt. rend.*, 1910, **151**, 342—344).—The flame of carbon disulphide burning in nitric oxide is shown to have a feeble sterilising action on water containing bacteria exposed to its light. Such a flame shows bands in the region λ 3400—4900 Ångström units, and it is to the rays of this part of the spectrum that the flame appears to owe its abiotic properties (compare Cernovodeanu and Henri, this vol., ii, 332). W. O. W.

Theory of Disinfection. REGINALD O. HERZOG and R. BETZEL (*Zeitsch. physiol. Chem.*, 1910, **67**, 309—313).—Silver nitrate is taken up by yeast as in a process of adsorption, and chloroform behaves similarly. In the case of formaldehyde, a constant amount is fixed by the yeast independently of the concentration. Phenol is not taken up by yeast. N. H. J. M.

Bactericide Value of Thymol. ERNST WILLY SCHMIDT (*Zeitsch. physiol. Chem.*, 1910, **67**, 412—432).—The action of thymol is very uncertain, and its employment in digestion experiments, especially those of long duration, with alkaline reaction should be discontinued. When animal and vegetable proteins are subjected to the action of a tryptic ferment in presence of thymol, misleading results may be obtained, owing to the bacteria attacking both the ferment and the protein. N. H. J. M.

Action of Anodic and Cathodic Liquids on Germination HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1910, 391—403. Compare this vol., ii, 232).—It has been shown previously (*loc. cit.*) that if wheat is allowed to germinate in contact with a $N/100$-solution of potassium chloride, through which an electric current is passed, the grain in the "anodic liquor" (that is, in that part of the solution near the anode) germinates less freely than that in contact with the "cathodic liquor," and the same difference is observed if wheat is allowed to germinate separately in such liquors, the electrodes having been removed, whence it is concluded that the effect of such liquors on germination is not due to electric charges on the ions, but to changes induced in the liquors by the passage of the current. In the present investigation an attempt is made to ascertain the nature of these changes, and the reasons for their influence on the germination of wheat. The initial salt solutions were centinormal in all cases. Filtration of the liquors has little influence. With sodium chloride or nitrate, cathodic liquor is more favourable to germination than anodic liquor, a mixture of the the two is intermediate, and an unelectrolysed solution is better than any of the other three. The same is true of potassium nitrate or chloride, except that in the former case the cathodic liquor is more favourable than the unelectrolysed solution as regards leaf formation. For mixtures of potassium and sodium chloride, the unelectrolysed solution is better than the cathodic liquor. Using Liege water, or water distilled in glass vessels, the cathodic liquor is more favourable than the anodic liquor, although for the distilled water the difference is slight.

It is unlikely that these results can be explained by Aso's work (this vol., ii, 439), although they may be accounted for by de Heen's suggestion, that the cathodic liquor contains ionic chains broken at negative points, since such chains may be more favourable to the germination of wheat than the ionic chains with positive ends, present in anodic liquors. Moulds (*Mucor*, spp.) always develop freely in the anodic liquors, whence it seems likely that the protoplasm of *Mucor* is different from that of the higher plants. T. A. H.

Origin of Osmotic Effects. III. The Function of Hormones in Stimulating Enzymic Change in Relation to Narcosis and the Phenomena of Degenerative and Regenerative Change in Living Structures. HENRY E. ARMSTRONG and E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1910, **82**, *B*, 588—602. Compare Abstr., 1909, ii, 387; this vol., ii, 668; also Guignard, Abstr., 1909, ii, 823; Mirande, Abstr., 1909, ii, 824).—When a leaf of cherry-laurel is exposed to the vapour of an anæsthetic, hydrogen cyanide is liberated; this is easily detected by means of Guignard's sodium picrate paper, and affords a delicate indication of the occurrence of enzymic change in the leaf. Not only the common anæsthetics, but most organic vapours, act as excitants, for example, toluene, benzene, naphthalene, carbon disulphide, volatile alcohols, and esters of acids of the acetic series, etc. Ammonia is very active, and carbon dioxide, benzaldehyde, and hydrogen cyanide also promote the change. Weak solutions of mineral acids, alkalis, and most salts are inactive, but the simpler organic

acids, mercuric chloride, cadmium iodide, and sodium and potassium fluorides all pass into the leaf from solutions. The behaviour of the laurel leaf resembles very closely that of the barley grain (compare A. J. Brown, Abstr., 1909, ii, 386). It is proposed to divide substances other than colloids into two sub-classes, according as they will or will not pass through differential septa, such as occur in the barley grain and the laurel leaf. The term "*hormone*," introduced by Starling, is applied to the former sub-class.

Experiments show that water actually passes into the leaf together with the hormone, and that not only is hydrogen cyanide liberated and water absorbed, but that the amount of reducing sugar in the leaf is greatly increased.

The hypothesis is advanced that when introduced into the living cell, substances generally which are not attractive to water exercise stimulative effects that are primarily mechanical, molecules of the hormone being interposed between the molecules in the cell by the change in the osmotic state and the activity of the medium raised, so that an influx of water from other regions takes place. Possibly the mere dilution thus effected is determinative of change; contact being established between hydrolyte and hydrolyst, degenerative changes are set up which tend to increase in intensity as the products of change (hydrogen cyanide and benzaldehyde) in turn exercise a similar stimulative influence; gradually enzymes are set free which can attack the various hydrolytes stored in the cell.

From this point of view, the phenomena of change in living structures, especially muscle and nerve, are considered, also the phenomena of narcosis, the regulation of respiration, and the physiological effect of alcohol and of drugs generally. The hypothesis also affords an explanation of a number of more recent observations on plant metabolism. E. F. A.

The Presence of Free Hydrogen Cyanide in Plants. CIRO RAVENNA and MARIO TONEGUTTI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 19—25).—Free hydrogen cyanide does not appear to be present in the leaves of the cherry-laurel, or occurs in them only in traces. This result is obtained when the leaves are immersed one by one in boiling water, so that the enzymes are destroyed instantaneously. When the destruction of the enzymes is less rapid, free hydrogen cyanide produced by their activity may be found, as, for instance, when a mass of leaves is placed in boiling water, the temperature of which is thereby reduced for a short time. That the acid may be formed in such a way is shown by the fact that mixtures of amygdalin and emulsin wrapped in paper yield it under these conditions. The leaves lose hydrogen cyanide to a much greater extent when dried slowly at the ordinary temperature than when the desiccation is carried out at 130° (compare Couperot, Abstr., 1909, ii, 257), but no hydrogen cyanide is evolved during the process. R. V. S.

Action of Vapours on Green Plants. MARCEL MIRANDE (*Compt. rend.*, 1910, **151**, 481—483. Compare Abstr., 1909, ii, 823; Mirande, *ibid.*, ii, 824; Heckel, this vol., ii, 63).—A large number of

substances are mentioned as producing blackening in the leaves of the cherry-laurel when the plant is submitted to the action of the vapours. In some cases liberation of hydrogen cyanide also occurs, whilst in others this is set free without blackening taking place. The compounds employed in the experiments included hydrocarbons and their halogen derivatives, alcohols, phenols, acids, ethers, esters, aldehydes, ketones, amides, amines, and nitriles. W. O. W.

The Betaines Present in Plants and Stachydrine. R. ENGELAND (*Zeitsch. physiol. Chem.*, 1910, **67**, 403—404).—Polemical (compare Schulze and Trier, this vol., ii, 743). The author claims priority in establishing the constitution of stachydrine, and also as regards the suggestion of the origin of betaines in vegetable tissues.

J. J. S.

Synthetic Production of Asparagine in Plants. DMITRI PRIANISCHNIKOFF and J. SCHULOFF (*Ber. Deut. bot. Ges.*, 1910, **28**, 253—264). —Pea seedlings supplied for thirteen days with ammonium chloride failed to produce asparagine, and the total nitrogen was not increased as compared with similar seedlings kept in water alone. Barley, on the other hand, showed a marked increase in total nitrogen, and produced a considerable amount of asparagine without reducing the amount of protein nitrogen.

When, however, calcium carbonate was added in addition to ammonium chloride, peas were able to take up nitrogen and to produce asparagine, and still better results were obtained when calcium sulphate was employed instead of carbonate. In the second experiment, the peas produced a small amount of asparagine from ammonium chloride alone, a result which is attributed to the somewhat higher temperature as compared with the earlier experiment.

If it should be shown that all the ammonia assimilated is converted into asparagine, it would follow that the latter is produced from malic (or fumaric) acid, and not from aspartic acid and ammonia.

N. H. J. M.

Enzyme Hydrolysing Aesculin and a Fat Splitting Enzyme in Aesculus hippocastanum. WILHELM SIGMUND (*Monatsh.*, 1910, **31**, 657—670).—Aesculin is hydrolysed to dextrose and aesculetin by an enzyme, *aesculase*, present in the bark, seed coats, and cotyledons of the horse chestnut (*Aesculus hippocastanum*), but not in the buds or leaves. Aesculase is without action on amygdalin. The cotyledons also contain a fat-splitting enzyme hydrolysing olive oil. E. F. A.

Constituents of Asparagus. J. LOUIS WICHERS and BERNARD TOLLENS (*J. Landw.*, 1910, **58**, 101—112).—The results of analyses of asparagus roots in April and July showed that both the main and the side roots contained considerably more sugar, and readily hydrolysed hemicellulose at the earlier than at the later period of growth. The main root contained more cellulose and furfuroids than the side roots and both contained more in July than in April. The percentage of

total nitrogen was considerably higher in the side roots than in the main roots, and increased from April to July in the former, remaining almost the same in the latter.

The main roots contained more ash and mere potash in April than the side roots, whilst in July the side roots contained more potash and about the same amount of total ash as the main roots. The amount of phosphoric acid was considerably higher in the side roots than in tho main roots, especially in July.

The results indicate that the organic constituents of asparagus cut from April to July are derived from the reserve substances of the roots, especially the thin side roots. N. H. J. M.

Carbohydrates of Asparagus. J. LOUIS WICHERS and BERNARD TOLLENS (*J. Landw.*, 1910, **58**, 113—116).—The expressed juice of asparagus was found to contain only reducing sugars (dextrose, 0·89%; lævulose, 1·55%), and no polysaccharides. Mannitol is probably present.

The roots contain dextrose and lævulose, and probably sucrose. Galactose was not found. N. H. J. M.

Presence of Stachyose (Manneotetrose) and of a Glucoside Hydrolysed by Emulsin in the Roots of Eremostachys laciniata. JOSEPH KHOURI (*J. Pharm. Chim.*, 1910, [vii], **2**, 211—213).—In a previous paper (this vol., ii, 151), the presence of a glucoside hydrolysed by emulsin in the leaves and twigs of this plant was announced. It is now shown that the roots also contain a glucoside of this type, and, in addition, stachyose, which was isolated in a pure state by Piault's method (Abstr., 1909, ii, 338). T. A. H.

Chemistry of the Higher Fungi. V. Maize Blight (Ustilago Maydis Tulasne). JULIUS ZELLNER (*Monatsh.*, 1910, **31**, 617—634. Compare Abstr., 1909, ii, 922).—The following substances were found to be present in ripe spores (collected in September) freed by sifting from the degenerated tissues: Ergosterol-like substances, oleic acid, solid and volatile fatty acids, lecithin, glycerol, resins (soluble and insoluble in light petroleum), sclerotic acid, phlobaphen, tannin, mannitol, erythritol, dextrose, trimethylamine, ustilagine, proteins, amanitin, an inverting ferment, a fat-decomposing ferment, an amorphous base, a carbohydrate soluble in alkali, and chitinous substances.

The spores contained 89·14% dry matter and 4·14% ash of the following composition:

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3, Al_2O_3.	Cl.	P_2O_5.	SO_3.	SiO_2.	C and loss.
52·02	0·40	1·74	3·90	1·04	4·33	17·96	4·49	4·44	6·63

N. H. J. M.

Chemistry of the Higher Fungi. VI. Relations of the Higher Parasitic Fungi and their Substrate. JULIUS ZELLNER (*Monatsh.*, 1910, **31**, 635—641).—The composition of the parasitic fungi depends, in the first place, on their systematic position,

and many of their chemical characteristics are shared by saprophytic fungi. Their composition is also influenced by the host plant; wood fungi contain diastases and maltase; maize blight an invertase, etc.

The fungi attack the host plant partly by means of ferments, which render soluble the insoluble constituents of the plant, and partly by the direct withdrawal of plant constituents. There is probably, in addition, secretion from the parasite, sometimes of harmless or even useful substances, and sometimes of toxic substances. N. H. J. M.

Occurrence of Organic Basic Substances in Yellow Boletus. K. YOSHIMURA (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 153—155).—The author has separated the following bases from a specimen of yellow boletus (*Boletus edulis*), 1 kilogram of the air-dried fungus being found to contain: adenine, 0·12 gram; histidine, 0·14 gram, and trimethylamine, 0·15 gram. Arginine and choline were not present. W. P. S.

Occurrence of Gentiopicrin in Roots and Stems of Gentiana pneumonanthe. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim*, 1910, [vii], **2**, 149—153).—Application of Bourquelot's methods of detecting glucosides and sugars in plants (Abstr., 1902, ii, 55; 1907, ii, 510) showed that the roots of this plant probably contained sucrose, gentianose, and possibly a third sugar, and indicated the presence of a glucoside, hydrolysed by emulsin. The glucoside was isolated by Tanret's method (Abstr., 1905, i, 655), and proved to be gentiopicrin (compare Abstr., 1910, ii, 234). The stems, bearing leaves and flowers, also contain sugar hydrolysed by invertase, and two glucosides hydrolysed by emulsin, one of which was isolated and proved to be gentiopicrin. T. A. H.

The Hellebore Group. I. OSCAR KELLER (*Arch. Pharm.*, 1910, **248**, 463—467).—*Nigella damascena* and *N. aristata* are the only members of the Nigella group which contain appreciable quantities of alkaloids; the former contains only damascenine, whilst the latter contains this alkaloid and its methyl and dimethyl homologues. On the assumptions that formaldehyde is the first assimilation product and that it can function as a methylating agent in the plant, the presence of the methylated alkaloids in *N. aristata* may be due to the greater development, the denser foliage, and the larger area of the leaves, factors which would condition a greater assimilative power, and therefore a more copious production of the first assimilation products, in *N. aristata* than in *N. damascena*. This idea, that the external form of plants, the greater or smaller development of their leaves, influences the composition of the alkaloids, and probably also of other substances, in the plants, is to be tested by an examination of members of other families. Obviously as many species as possible of a family must be examined, and a knowledge of all the bases therein be obtained. The groups of the family Ranunculaceæ have been selected, and are classified according as they are non-poisonous, poisonous but free from alkaloids, or contain alkaloids. At present the author is dealing with the groups *Helleborus*, *Aquilegia*, *Caltha*, and *Delphinium*; the

alkaloids in plants of the last group are of especial interest (see following abstract). C. S.

The Hellebore Group. II. New Delphinium Bases. OSCAR KELLER (*Arch. Pharm.*, 1910, **248**, 468—475).—The seeds of *Delphinium staphysagria* have long been known to be poisonous and to contain an alkaloid. The author now finds that the seeds of *D. consolida* contain at least three alkaloids. The seeds are extracted four times for four to eight days with 95% alcohol containing 0·5% hydrogen chloride. The extracts are concentrated and water is added, the pasty precipitate is removed, and the filtrate, after being concentrated on the water-bath, is extracted with chloroform-ether, the extraction being repeated after the solution has been basified. The crude bases removed from the chloroform-ether extracts by 5% hydrochloric acid are isolated as the hydrochlorides, a solution of which, after being basified with ammonium hydroxide, is extracted with ether and with chloroform; the ethereal solution slowly deposits large, hexagonal prisms of a substance *A*. The ammoniacal filtrate is neutralised by hydrochloric acid, basified by sodium hydroxide, and again extracted with ether and with chloroform, whereby a further quantity of crystalline matter, apparently identical with *A*, is obtained. The amorphous substance recovered from the ether and the chloroform can be separated into two portions, one soluble, the other insoluble, in ether. These portions, which are probably mixtures, have not yet received further attention.

The substance *A* separates from alcohol in colourless, hexagonal plates, m. p. 195—197°, reacts strongly alkaline in solution, does not form crystalline salts, acts as a very powerful poison when injected into cold-blooded animals, and resembles, but certainly is not identical with, Merck's delphinine *pur. crystallisat.* The latter is shown, by crystallisation from alcohol and mechanical separation, to be a mixture of a substance, m. p. 187·5°, crystallising in hexagonal plates, and another substance, crystallising in tufts of short needles, which softens at 187° and darkens, but is not fused, at 250°. C. S.

Chemical Examination of the Tuberous Root of Ipomœa horsfalliæ. FREDERICK B. POWER and HAROLD ROGERSON (*Amer. J. Pharm.*, 1910, **82**, 355—360. Compare Abstr., 1908, ii, 725; 1909, i, 819).—The root, dried in a water-oven and ground, yielded by extraction with hot alcohol 2·5% of a dark brown, spongy resin, having $[\alpha]_D$ $-28·4°$ in alcohol, after decolorisation by animal charcoal. On successive extraction with (1) light petroleum, (2) ether, and (3) alcohol, it furnished the following three fractions: (1) a soft brown resin, containing (*a*) a *substance*, m. p. 132—133°, giving the colour reactions of a phytosterol, and (*b*) a mixture of unsaturated oily acid, with a crystalline *acid*, m. p. 56—58°; (2) a soft brown resin containing (*a*) probably a dihydric alcohol of the ipuranol type (*loc. cit.*); (*b*) resins, soluble in sodium carbonate or hydroxide; (3) resin containing some glucosidic material.

The crude alcoholic extract referred to above yields on steam-distillation traces of formic and butyric acids, whilst that portion (non-

resinous matter) soluble in water contained (*a*) traces of a fluorescent substance, probably β-methylæsculetin, already shown to occur in jalap resin (Abstr., 1909, i, 819), and (*b*) a sugar yielding *d*-phenylglucosazone and indefinite extractive matter precipitated by lead acetate. The root also contained much starch. T. A. H.

The Occurrence of Hemicellulose in the Pods of Pisum sativum and Phaseolus vulgaris. ERNST SCHULZE and U. PFENNINGER (*Zeitsch. physiol. Chem.*, 1910, **68**, 93—109).—The nitrogen-free extract of the pods both of *Pisum sativum* and of *Phaseolus vulgaris* is rich in hemicellulose, and the amount increases as maturation advances; thus the dried, unripe pods of Pisum contained 16—19% of hemicellulose, while in the ripe pods the amount was 48·6%. On hydrolysis, galactose and arabinose are obtained. Full details of the hydrolysis are given, but the hemicellulose was not actually isolated. E. J. R.

Glucoside of Pyrola rotundifolia. Mlle. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1910, [vii], 2, 193—203. Compare Abstr., 1908, ii, 995, and this vol., ii, 742).—By the application of Bourquelot's biological method, it was ascertained that this plant contained sucrose and a glucoside hydrolysed by emulsin, which was probably arbutin. The latter was isolated in a crystalline condition and identified. The slight differences between this preparation and pure arbutin were probably due to the presence of traces of impurity (methylarbutin ?). The plant also contains invertase and emulsin. The quantity of sucrose in the plant is about three times as great in January and February as in May, but the proportion of glucoside remains unchanged. The plant can be dried without material change in the quantity of glucoside and sucrose present. T. A. H.

Influence of Copper and Manganese Sulphates on the Growth of Barley. W. E. BRENCHLEY (*Ann. Bot.*, 1910, **24**, 571—583).—Water-culture experiments in which barley plants were grown in solutions containing copper and manganese sulphate respectively in addition to the usual nutrients.

In the case of copper sulphate, it was found that in solutions containing from 20 down to 4 mg. of the crystallised salt per litre growth was checked in nearly every case, whilst 0·2 mg. per litre was without effect. No stimulating action was observed.

The results obtained with manganese sulphate indicate that whilst not actually toxic, like copper sulphate, moderate amounts of the salt considerably retard growth. Smaller amounts (10 mg. of the crystallised salt per litre, and less) seem to have a stimulating action.

N. H. J. M.

Fluorine in Wines. A. KICKTON and W. BEHNCKE (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 193—208).—The authors have detected the presence of fluorine in many different kinds of wines; one hundred and thirty-nine samples, consisting of Spanish, Portuguese, Italian, Greek, Turkish, Cape (S. Africa), French, German, and other wines, were examined, and in most cases a positive reaction was obtained.

Vandam's test (Abstr., 1908, ii, 63) was found to afford the most trustworthy means of detecting the presence of fluorine compounds; when more than 1 milligram of fluorine is present in the quantity of wine used in the test, the depth of the etching is not a measure of the amount of fluorine, but if the etching is only rendered visible when the glass is breathed on, it may be concluded that less than 1 milligram of fluorine is present per 100 c.c. of wine. One Portuguese wine and about one-half of the number of Spanish wines examined contained very appreciable quantities of fluorine compounds; estimated by Treadwell and Koch's method (Abstr., 1904, ii, 841), the amounts found, calculated as sodium fluoride, varied from 4·6 to 11·1 milligrams per 100 c.c. of wine. These figures, in spite of the fact that the method was found to give too low results, indicate that certain Portuguese and Spanish wines contain added fluorine compounds, or that the wines have become contaminated by being stored in casks which have been treated with fluorides and insufficiently washed (compare Abstr., 1908, ii, 318). W. P. S.

Occurrence of Arsenic in Soils, Plants, Fruits, and Animals. WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1910, 9, 345—360).—Arsenic, in a form which is slightly soluble in water, is widely distributed in the virgin soils of Colorado, especially in those which are marly, the amount varying from 2·5 to 5·0 parts per million. The marl underlying the soil is rather richer in arsenic, the quantity present ranging from 4 to 15 parts per million.

Soils on which crops have been grown which have been sprayed with arsenic preparations contain from 10 to 28 times as much arsenic as the virgin soils. Alfalfa, oats, potatoes, apples, and pears grown on such soils contain arsenic, which element is also found in the flesh and kidneys of animals which have been fattened on such alfalfa. It is also found in the urine of persons who have partaken freely of the apples grown on sprayed trees. T. S. P.

Transformation of Calcium Cyanamide in Soil. III. CELSIO ULPIANI (*Gazzetta*, 1910, 40, i, 613—666. Compare Abstr., 1908, i, 859).—The views now advanced by Löhnis (compare Löhnis and Moll, Abstr., 1909, i, 92) are in substantial agreement with those put forward by the author, except that they suppose the first product of hydration to be ammonium cyanate, which is then converted into carbamide, whilst the author considers that the latter is formed directly It is further pointed out that the idea that the transformation is effected by bacteria in the soil has now been generally abandoned, except by Kappen. In the author's opinion, however, the results of the latter are vitiated by the fact that in his experiments the presence of certain compounds (amino-acids, aldehydes) was not excluded, and these substances yield compounds with cyanamide which no longer give the reactions of cyanamide. Continuing his work on the subject, the author confirms his previous statement that the transformation of cyanamide in contact with soil proceeds in two stages, the cyanamide being first converted into carbamide, which is then transformed into ammonium carbonate. It has been found possible to isolate the

carbamide, and to estimate the ammonia formed. From an examination of the rate at which cyanamide is transformed when solutions of it at various concentrations are kept in contact with soil at different temperatures, it follows that in the first stage no micro-organisms are involved, for the following reasons: (1) the conversion proceeds most rapidly when the substances are first brought together, and it afterwards gradually diminishes; (2) the amount converted, increases with the concentrations of the solutions taken. and also proceeds in the same way at concentrations incompatible with life; (3) the conversion also takes place in the presence of antiseptics and with sterilised materials, and proceeds with increased velocity at 100°; (4) sterilised charcoal converts cyanamide solutions into carbamide in the same circumstances as soil, although it is uncertain whether the further transformation into ammonia can be effected in this way. When the colloidal properties of soil are destroyed by heat or by the action of acids or alkalis, it loses the property of converting cyanamide solutions into carbamide, but acquires it again when mixed with colloidal substances, such as precipitated silicic acid, aluminium hydroxide, ferric hydroxide, aluminium silicate, and the amorphous hydrated silicates (zeolites) found in soils. It is probable that the colloids act catalytically on account of the large surface they present. The transformation is the more rapid the greater the surface of contact between soil and solution becomes. The conversion of the cyanamide is accomplished in two stages: in the former an accumulation of the substance takes place in the bounding layer between liquid and solid (corresponding with the rapid absorption during the first fifteen minutes), whilst in the second stage the actual decomposition of the material in this layer occurs. The question of the possible intervention of micro-organisms in the conversion of the carbamide into ammonia remains undecided. The ammonia formed is absorbed by the soil, and its disappearance naturally accelerates the reaction. It has been further found that the presence of soil, not only affects the rate of conversion of calcium cyanamide, but also alters its character, for whereas a solution of cyanamide tends to polymerise into dicyanodiamide, the same solution under the same conditions when in contact with soil yields no dicyanodiamide, but is converted into carbamide. R. V. S.

Effect of Carbon Disulphide on Decomposition Processes in Soils. RICHARD SCHERPE (*Bied. Zentr.*, 1910, **39**, 509—522; from *Arb. k. biol. Anstalt Land-, Forstwirts*, 1909, **7**, 353).—Pot and field experiments on the effect of carbon disulphide applied to soil alone and to soil manured with leather meal, green manure, and lime respectively. The results showed an increase in readily soluble forms of nitrogen in the soil under the influence of carbon disulphide, but failed to show whether leather meal was more rapidly broken down. In the case of green manure (potato leaves), treatment with carbon disulphide had no appreciable effect for two and a-half months, after which the soil so treated became distinctly darker in colour than the soil which had no carbon disulphide, and showed a strongly alkaline reaction.

On limed soil carbon disulphide had much less effect. This is

attributed to the production of a double compound of calcium thio-carbonate and hydroxide, which in time would be converted into polysulphides and then into hydrogen sulphide or injurious organic sulphur compounds. N. H. J. M.

Analytical Chemistry.

Explosion Indicator. NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], **82**, 237—240).—An apparatus is figured and described, whereby the existence of an explosive gaseous mixture can be detected at a distance. The tube through which the gas is drawn by a pump bifurcates. One limb of the bifurcation consists of a glass explosion vessel, 15 c.c. in volume, closed at each end by stopcocks and provided with the usual platinum explosion wires. Sealed into the side of the vessel is a tube, provided with a stopcock and communicating with the atmosphere. Resting against the open end of this tube is a pendulous iron disk. The gaseous mixture under examination is drawn through the apparatus, the stopcocks at each end of the explosion vessel are then closed, the spark is passed, and the stopcock of the side-tube opened, whereupon the pressure in the explosion vessel, provided that an explosion has occurred, drives the pendulous iron disk against an electromagnet, thereby completing a circuit and sounding an alarm-bell at any desired place. C. S.

Improved Mouth-Blowpipe. L. S. BAGSTER (*Chem. News*, 1910, **102**, 89—90).—The blow-pipe is provided with a sliding two-way tap so that the air supply may be directed either to the blowpipe itself or, through a length of flexible tubing, into the glass tubing which is being heated by the blowpipe. W. P. S.

Siphon for Use with Carboys. EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1910, **24**, 327—328).—The siphon described is intended for use with concentrated acids, etc., and in other cases where it is inconvenient to start the action of the siphon by aspiration. The upper portion is made horizontal, and a cup or funnel, fitted with a three-way tap, is provided on this horizontal part near the point where it joins the vertical tube forming the short arm of the siphon; a short stoppered side-tube is provided at the top of the long arm of the siphon, and the lower end of this arm is fitted with a tap. The short arm of the siphon is placed in the carboy to be emptied, and some of the liquid from the latter is run into the cup and allowed to fill the long arm, the three-way tap being turned so as to allow of this being done; the tap at the lower end of the long arm is closed meanwhile. The stopper is then inserted in the short side-tube, the three-way tap is turned so as to connect the two arms and cut off the cup, and the siphon commences to work when the lower tap is opened. Should

there be but little liquid in the carboy, it may be necessary to repeat this operation of filling the siphon before it will work satisfactorily.

W. P .S.

Modified Burette for Standard Alkali Solutions. PAUL RUDNICK (*J. Amer. Chem. Soc.*, 1910, **32**, 971).—Glass-stoppered burettes are objectionable for use with alkali hydroxide on account of the tendency of the stopcock to stick, the rapid wear which causes the tap to leak or break, and other disadvantages. The use of a glass tip connected to the burette by means of rubber tubing carrying a spring-clip is liable to introduce error.

The author has therefore employed a burette with a silver stopcock, and this has been found quite satisfactory. After it had been used for 30% sodium hydroxide for several weeks, it was still in as good a condition as when first received. E. G.

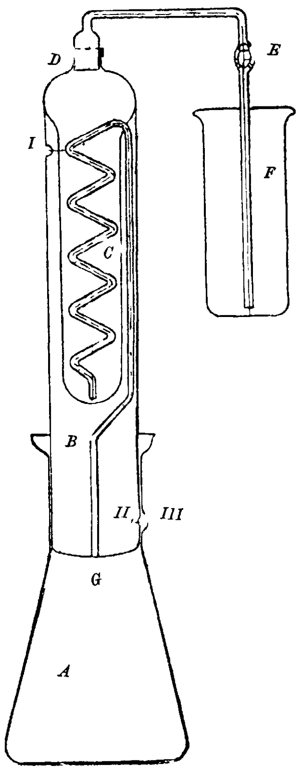
Apparatus for Gas Volumetric Determinations. W. MÜLLER (*Zeitsch. angew. Chem.*, 1910, **23**, 1556).—A simple and convenient apparatus is described for measuring the volume of gas liberated during a reaction. The gas expels water from a receiver which is so arranged that the water level is readily adjusted when the reaction is at an end. The volume of gas liberated is determined from the volume or weight of water expelled from the apparatus. T. S. P.

New Laboratory Apparatus. THEO GRZESCHLK (*Chem. Zeit.*, 1910, **34**, 949).—The gas-washing bottle constructed by Adämmer, in which the gas current is forced through two sieve-like plates, and consequently gets into a fine spray, is recommended. A rapid filtering arrangement in connexion with the water-air pump is described. It consists of a funnel holder fitted with a side-tube and three interchangable ground funnels; the holder is placed on any suitable flask fitted with a rubber cork. A condensed drop-catcher to prevent any liquid from passing into the absorption liquid is next described. It consists of a pipette-shaped glass, into the upper end of which is sealed a horn-shaped tube. Just opposite the end of this tube the wall of the bulb is pressed inwards, and this causes the drop to flow down the side of the pipette. L. DE K.

A Convenient Condenser. ARNOLD HAHN (*Chem. Zeit.*, 1910, **34**, 809).—The apparatus is intended for the distillation of small quantities of liquids. The outer tube, resembling an ordinary condenser, is enlarged at the upper end to a bulb. The inner tube consists of the lateral tube of the distilling flask. The condenser, which is filled through the large opening in the bulb, is large enough to hold an amount of water sufficient to keep it cool during a distillation lasting for about half an hour, and if necessary iced water may be used. By means of a rubber tube with a clamp, the water may then be drawn off at the lower end. L. DE K.

Apparatus for the Estimation of Sulphur [in Iron, etc.] GEORG PREUSS (*Chem. Zeit.*, 1910, **34**, 840).—In the accompanying

illustration, *A* is the flask used for the introduction of the sample and the acid, and *B* is the condenser attached to the flask by means of a ground joint. In the upper part of *B* is found a 5 mm. circular opening, *I*, and a similar one at the lower end near *II*. Above the opening *II* in the flask *A* is found a rabbet, *III*. In the condenser *B* is placed a vessel *C*, which is half filled with water, which serves to absorb hydrochloric acid fumes, and *D* is a ground, hollow glass stopper which ends in a bent tube. Inside is placed a ground recoil valve *E*, which leads to the absorption vessel *F* containing cadmium solution. The tube *G* attached to the flask *A* conducts the gases through *B*, penetrates into the condensing vessel *C*, and, assuming a serpentine form, leads nearly to the bottom of the vessel; the hydrochloric acid fumes are thus completely condensed before reaching *F*. The recoil valve *E* prevents any regurgitation of the liquid in the absorption vessel *F*. *B* is filled with cold water, containing 50 grams of sodium hydrogen carbonate per litre, through the opening *I* by means of a wash-bottle.



After the operation is finished, the cooling water is emptied into the flask *A* by turning the condenser with opening *II* on to the rabbet *III* of the flask. The carbon dioxide evolved removes the last traces of hydrogen sulphide from the flask into the absorption liquid.

L. DE K.

Estimation of Total Sulphur in Organic Matter. HERMAN SCHREIBER (*J. Amer. Chem. Soc.*, 1910, **32**, 977—985).—The peroxide method of estimating sulphur in organic substances is not altogether satisfactory for the following reasons. The amount of peroxide added varies with the material analysed and the rate at which it is added. The amount of acid added after fusion also varies in each case, and the solution must therefore be made alkaline again and re-acidified. Moreover, the fusions are liable to burn and blow out of the crucible. In view of these objections, the following method has been devised.

One gram of the material to be analysed is placed in a 100 c.c. nickel crucible, and 10 c.c. of a solution, containing 100 grams of sodium nitrate and 150 grams of sodium hydroxide in 500 c.c., are added. Five grams of crystalline magnesium nitrate are introduced and stirred with a platinum rod. The stirring rod and the sides of the crucible are washed down with the smallest possible quantity of water, and the crucible is then heated at 130° for an hour, and afterwards at 150—160°,

until the contents are dry. After the cover has been put on tightly, the temperature is raised gradually to 180° and the crucible is heated for thirty-five minutes at 180—200°, and afterwards with the Bunsen burner for half an hour. When the fused mass has solidified, the crucible is placed in a 600 c.c. beaker with 150 c.c. of water. Hydrochloric acid (13 c.c. of D 1·19) is now added, and the crucible is washed out with water. The beaker is heated for half an hour, and left in the cold during the night. The liquid is then filtered, and the residue washed. The filtrate is heated, and precipitated with 10% barium chloride solution.

The results obtained in a series of analyses of various materials by this method are compared with those obtained by the peroxide method. This comparison shows that the former method gives results about 0·1% lower than the latter, or about 0·064% lower than would be obtained by the absolute method. Both these discrepancies are well within the limits of experimental error.

In order to determine the effect of the salts in solution on the precipitation of the sulphate, comparative experiments were made by the new method and the peroxide method, in which definite volumes of dilute sulphuric acid were added to the solutions, blank experiments being carried out simultaneously. It was found that the new method gives results 0·1% too high when 3·5% of sulphur is present, and 0·3% too high when 8% of sulphur is present. E. G.

Gravimetric Estimation of Sulphuric Acid in the Presence of Alkali Metals. YOGORO KATO and ICHISABURO NODA (*Mem. Coll. Sci. Eng. Kyōtō*, 1909—1910, **2**, 217—228).—The concentration of a semi-normal solution of sulphuric acid was determined gravimetrically both in the absence of, and in the presence of, equivalent solutions of the chlorides of potassium, sodium, and ammonium. Determinations were also made with varying concentrations of the haloid salts, and with more dilute solutions of sulphuric acid.

Potassium chloride caused the greatest error in the determination. The ratio (R) of salt to acid and the percentage difference (D) between the results obtained in the absence of, and in the presence of, potassium chloride are connected by the equation: $\log D = n\log R + K$, where K is a constant. This is similar to the ordinary adsorption formula, so that it is probable that potassium sulphate is adsorbed during the precipitation of the barium sulphate.

Adsorption is diminished, but not completely, by diluting the solution. No adsorption takes place in the presence of magnesium chloride. T. S. P.

Apparatus for the Estimation of Arsenic. OTIS D. SWETT (*J. Amer. Chem. Soc.*, 1910, **32**, 962—965).—A new form of apparatus suitable for the estimation of arsenic by the Marsh-Berzelius, Gutzeit, and similar methods is described with the aid of a diagram. The chief advantages claimed for it are that it consists of fewer parts than most of the existing forms, and, whilst giving trustworthy results, is compact and portable. E. G.

Precipitation of Arsenic Acid by Ammonium Molybdate. G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 15—19).—The author has investigated the conditions requisite for the quantitative precipitation of arsenic acid by ammonium molybdate in neutral and in acid solutions of different strengths. When precipitation is effected in solutions containing mineral acid, and having an acidity greater than 0·030% of hydrogen ions, the precipitate is yellow. Ammonium nitrate must be present, and the requisite quantity of ammonium molybdate depends on the concentration of the solution and its degree of acidity.

Precipitation is complete under the following conditions: 10 c.c. of a solution containing 0·080 gram of arsenic oxide are treated with 15 c.c. of a solution of ammonium nitrate containing 370 grams per litre, then with 60 c.c. of water and 2·5 c.c. of concentrated nitric acid (D 1·30); the liquid is boiled, and 1·60 grams of solid ammonium molybdate are added, the boiling being continued for three minutes. The precipitate is washed by decantation with a solution containing 50 grams of ammonium nitrate and 40 c.c. of nitric acid per litre.

In the case of neutral solutions and of solutions containing mineral acids, but having a smaller acidity than that given above, similar conditions are recommended. The precipitate obtained is white, and the washing is effected with a solution of ammonium nitrate, in which it is practically insoluble.

In the presence of organic acids (tartaric, oxalic, citric, acetic, succinic, and phthalic acids were employed) the white modification is usually precipitated. A large excess of ammonium molybdate is necessary.

Analysis of the yellow precipitate gave the value 1 : 24·34 for the ratio $As_2O_5 : MoO_3$ in it, whilst for the white modification the ratio was found to be 1 : 16·10. R. V. S.

Detection of Arsenic Acid in Presence of Phosphoric Acid. G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 68—69).—The solution of the alkali salts of the two acids, rendered faintly acid with acetic acid and reduced to a small volume, is treated with 10—15 c.c. of a concentrated solution of ammonium nitrate, and when the mixture has been raised to boiling point about 1 gram of solid ammonium molybdate is added. When this has dissolved, the liquid is boiled for about one and a-half minutes. If arsenic acid is present, a white precipitate is formed. By this method 0·002 gram of arsenic acid can be detected in the presence of a large quantity of phosphoric acid. Salts of calcium, strontium, and magnesium do not invalidate the test, but render it rather less delicate. R. V. S.

Rapid Estimation of Carbon in Steel and Other Iron Alloys. R. AMBERG (*Chem. Zeit.*, 1910, **34**, 904).—Johnson's process, which consists in burning the alloy in a current of oxygen, as a rule without addition of any oxidising substance, and using a quartz combustion tube, is recommended (compare Abstr., 1906, ii, 630; 1908, ii, 630).

L. DE K.

Apparatus for the Determination of Equivalents of Metals and for the Estimation of Carbon Dioxide both Directly and Indirectly. MANINDRA NATH BANERJEE (*Chem. News*, 1910, **102**, 90—92).—The apparatus consists of a small flask fitted with a cork, through which pass the stem of a small tapped funnel, a short bent tube, and a delivery tube. The portion of the latter below the cork is provided with three bulbs, and the lower end is bent upwards so as to be level with the uppermost bulb. Concentrated sulphuric acid is filled into these bulbs, and serves to dry the gases liberated from the substance contained in the flask by the action of a reagent (sulphuric acid, etc.) introduced from the tapped funnel. The gases evolved may be collected in a suitable absorption tube and weighed, or their quantity determined by weighing the apparatus before and after the operation. A small hand-bellows and a drying tube are provided for passing a current of air through the apparatus to remove residual traces of gases. W. P. S.

Analysis of Amblygonite. H. CORMIMBŒUF (*Ann. Chim. anal.*, 1910, **15**, 295—298).—The following method is recommended for the analysis of amblygonite, which is, essentially, lithium sodium fluorophosphate. Two grams of the finely divided sample are mixed in a platinum crucible with 4 grams of calcium oxide, and then heated over a blast-lamp for about fifteen minutes. When cold, the semi-fused mass is dissolved in dilute nitric acid, and the solution is evaporated to dryness. The silica is collected on a filter, and the phosphoric acid is estimated in the filtrate by the bismuth method. After removing the excess of bismuth (as sulphide) in the filtrate from the bismuth phosphate precipitate, the aluminium is precipitated in the usual manner. The filtrate from the aluminium hydroxide is treated with ammonium oxalate to remove calcium salts, and the sodium and lithium remaining in the solution are weighed together as their sulphates. The lithium is finally separated from the sulphate mixture as its phosphate. The fluorine is estimated by difference. W. P. S.

Separation of Calcium and Magnesium. ERNST MURMANN (*Zeitsch. anal. Chem.*, 1910, **49**, 688—698).—Calcium may be separated with sufficient accuracy from magnesium by the oxalate process in its various modifications, either in ammoniacal or acetic acid solutions. If, however, as in the case of magnesite, the magnesium largely predominates, the results are quite erroneous.

Attempts to remove the magnesium by means of barium hydroxide and then to estimate the calcium in the filtrate, after precipitating the barium with sulphuric acid, proved quite unsuccessful even when dealing with extremely dilute solutions.

The only successful way of obtaining a complete separation is to prepare a solution of the mixed chlorides in 90% alcohol. The amount of calcium should be approximately known, and a sufficiency of dilute sulphuric acid be added to secure its conversion into sulphate. The precipitate is then freed from any co-precipitated magnesium sulphate by prolonged washing with the same alcohol. L. DE K.

Estimation of Barium. MAURICE HUYBRECHTS (*Bull. Soc. chim. Belg.*, 1910, **24**, 281—283. Compare this vol., ii, 544) —Results of experiments are given which appear to indicate that the estimation of barium as sulphate is most trustworthy when the solution from which the precipitation is made contains about 0·5% of free hydrochloric acid; it is also advisable to use a considerable excess of the precipitant (10% ammonium sulphate solution). W. P. S.

Estimation of Small Quantities of Lead in Alloys of Antimony, Copper, and Tin. WOLFGANG MANN (*Chem. Zeit.*, 1910, **34**, 917).—Ten grams of the alloy are dissolved in 45 c.c. of hydrochloric acid, D 1·19, and 5 c.c. of nitric acid, D 1·4, 10 grams of tartaric acid are added, and the whole is diluted to 300 c.c. When cold, ammonia, D 0·91, is added until the liquid is about neutral, when another 100 c.c. of ammonia are added. Enough potassium cyanide solution is added until the liquid is colourless, and another extra 5 grams of solid cyanide are introduced. After heating to 70°, a rapid current of hydrogen sulphide is passed. The impure lead sulphide is collected, and washed with a hot solution of ammonium sulphide and potassium cyanide (50 grams of commercial ammonium sulphide and 10 grams of potassium cyanide in a litre of water; the liquid is heated until colourless). The sulphide is then dissolved in hydrochloric acid containing bromine, the bromine is boiled off, and, when cold, excess of ammonia is added, and also 5 grams of potassium cyanide. The lead is now re-precipitated as sulphide, which is then redissolved in hydrochloric acid and bromine, and converted into sulphate by evaporating with addition of 10 c.c. of 50% sulphuric acid.

After weighing the lead sulphate as usual, it should be boiled repeatedly with ammonium acetate, and any insoluble residue be allowed for. L. DE K.

New Reaction for Copper. RUDOLF UHLENHUTH (*Chem. Zeit.*, 1910, **34**, 887) —The reagent is prepared by dissolving 0·5 gram of 1 : 2-diaminoanthraquinone-3-sulphonic acid in 500 c.c. of water with addition of 40 c.c. of aqueous sodium hydroxide, D 1·4. On adding the reagent to a solution of a copper salt so dilute that the usual tests fail to detect it, there will still appear a blue coloration. The test seems to be conclusive for copper. L. DE K.

Electro-deposition of Metals. F. MOLLWO PERKIN and WILLIAM E. HUGHES (*Trans. Faraday Soc.*, 1910, **6**, 14—18. Compare Sand, Trans., 1907, 373).—The authors describe the various forms of rotating anode and cathode which they have tried for rapid electro-deposition of metals. In the most satisfactory apparatus, the anode is a closely-wound spiral of iridio-platinum wire, rotating at 750—950 revolutions per minute within a fixed cathode, consisting of a cylinder of fine platinum gauze. The whole is placed in a tap funnel with a side-tube in which a capillary electrometer can be dipped when potential measurements are desired. With this apparatus, 0·03735 gram of cobalt or 0·1265 gram of copper can be satisfactorily deposited in ten minutes. In making potential measurements, the apparatus described

by Sand is used in conjunction with a potentiometer and mirror galvanometer, a $10N$-solution of ammonium nitrate being used as connecting solution. In depositing cobalt, the potential break occurs at 0·2 volt, with copper at 0·55 volt. With very low potentials, cobalt oxide may be deposited on the anode. R. J. C.

Estimation of Copper as Anhydrous Cupric Sulphate. ALBERT RECOURA (*Bull. Soc. chim.*, 1910, [iv], 7, 832—834).—Although the last traces of water are only removed with great difficulty from copper sulphate at 180—200° when the latter is a residue from a neutral aqueous solution, it is found that such a residue from a solution containing a little sulphuric acid can be freed easily from water and the excess of acid at this temperature. It is suggested that by taking advantage of this fact, all copper compounds which can be readily converted into cupric sulphate, directly or indirectly, may be estimated as anhydrous cupric sulphate. T. A. H.

The Separation of Copper from Cadmium and Zinc by means of "Cupferron." JOSEF HANUŠ and ARN. SOUKUP (*Zeitsch. anorg. Chem.*, 1910, 68, 52—56).—The results obtained agree with those of Biltz and Hödtke (this vol., ii, 550). The separation of copper from cadmium and zinc by means of this reagent has no advantage over the older methods. C. H. D.

Colorimetric Estimation of Manganese in Presence of Iron. M. R. SCHMIDT (*J. Amer. Chem. Soc.*, 1910, 32, 965—967).—An account is given of the best mode of carrying out Walter's colorimetric method for estimating small quantities of manganese in presence of iron (*Chemical News*, 1901, 84, 239) so as to obtain accurate results with as great rapidity as possible. The method has been found suitable for estimating manganese in certain pharmaceutical preparations. It has been employed by Hillebrand in the analysis of minerals, and should also prove useful for the estimation of manganese in waters. E. G.

The Part taken by Atmospheric Oxygen in the Oxidation of Oxalic Acid by the Higher Oxides of Manganese. K. SCHRÖDER (*Zeitsch. öffentl. Chem.*, 1910, 16, 270—283, 290—305).—When the available oxygen in pyrolusite is estimated by Lunge's method, the results are high if the hot solution is allowed to remain before titrating back. Air alone is without action on oxalic acid, the presence of a manganese salt being necessary. The oxidation is still further accelerated if titanium is present as well as manganese. By excluding air, or by using a concentrated solution of oxalic acid and heating rapidly, results may be obtained which agree with those given by titration with ferrous sulphate.

In titrating oxalic acid with potassium permanganate, a small error arises from induced atmospheric oxidation if the titration is slow (five to ten minutes) and the solution is only slightly acid. This error is increased by the presence of manganese sulphate, and still more by titanium dioxide. Such additions give rise to error, even in strongly acid solutions titrated rapidly.

The formation of hydrogen peroxide, observed by Georgevics and Springer (Abstr, 1900, ii, 631) and by Skrabal (Abstr., 1905, ii, 17, 18), also occurs when oxalic acid acts on manganese dioxide, and depends on the action of atmospheric oxygen, as it is not observed in the absence of air. When the titration of oxalic acid with permanganate is rapid, there is a compensation of errors, as the results are not low even when a stream of oxygen is passed through the apparatus. This must be attributed to the formation of hydrogen peroxide. The peroxide is only very slowly decomposed, even on boiling, by oxalic acid, except in the presence of titanium or of much manganese.

For practical purposes, the error of the titration is negligible, even in contact with air, if the temperature is not above 50°, and the solution contains as much as 30 c.c. of sulphuric acid (1 : 1) to 200 c.c. of water, and the titration is performed rapidly. It is therefore best to determine the approximate quantity of permanganate required by a preliminary titration, and then to warm the solution to 50° and add the greater part of the permanganate at once. The addition of a manganese salt is undesirable.

The author also reviews the theory of the induced reaction.

C. H. D.

Sulphurous Acid as an Etching Reagent for Metallographic Purposes. SIEGFRIED HILPERT and EDWARD COLVER-GLAUERT (*Zeitsch. anorg. Chem.*, 1910, **68**, 63—68).—A dilute solution of sulphurous acid (1 : 25) reacts with iron, coating the surface with a thin layer of sulphide. This reaction may be used to develop the structure of cast iron and steel. Cementite is not attacked. The results obtained on etching austenite, martensite, and troostite differ somewhat from those given by other reagents, and the method may prove useful in distinguishing these constituents. C. H. D.

Precipitation of the Iron Group and the Composition of Certain Ferric Formates. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1910, **32**, 953—957).—The precipitation of iron, aluminium, and chromium as basic acetates is not very satisfactory, on account of the difficulty of filtering and washing the precipitate. Schulze (*Chem. Centr.*, 1861, 3) therefore recommended the use of ammonium formate for precipitating iron and aluminium, and this method has been studied by the author.

It has been found that both iron and aluminium can be completely precipitated by boiling with ammonium formate if the solution is sufficiently dilute. Filtration takes place more rapidly than in the case of the basic acetates. Chromium is not precipitated unless iron is present. The presence of ammonium chloride is desirable, as it causes the precipitate to form larger flakes and thus facilitates filtration. The method of procedure which has been found to give the best results is described in detail.

Ludwig (*Arch. Pharm.*, 1861, [ii], **107**, 1) and Scheurer-Kestner (*Compt. rend.*, 1863, **56**, 1092) have stated that ferric triformate can be prepared by the action of formic acid on moist ferric hydroxide.

It is now found, however, that the product thus obtained has the composition $Fe_3(OH)_2(CHO_2)_7$. The basic formate precipitated under the usual conditions is represented by the formula $Fe_3O_3(OH)_2 \cdot CHO_2$.

E. G.

Pyrogallol Dimethyl Ether, a Delicate Reagent for Chromic Acid, Ferric Salts, and Nitrites. JULIUS MEYERFELD (*Chem. Zeit.*, 1910, **34**, 948).—If a 2% aqueous solution of the reagent is added to a solution of potassium dichromate acidified with sulphuric acid, a yellowish-red or, in very weak solutions, a yellow coloration is formed. Chloroform extracts the colouring matter and turns yellow. This test exceeds in delicacy the hydrogen peroxide test.

As a test for iron it is about equal to the thiocyanate test, and in the case of nitrites it is about as delicate as the reaction with potassium iodide and starch. The test is also obtained with potassium permanganate so diluted as to be colourless. It is essential that the reagent should be freshly prepared.

L. DE K.

Rapid and Accurate Method for the Estimation of Titanium. O. L. BARNEBEY and R. M. ISHAM (*J. Amer. Chem. Soc.*, 1910, **32**, 957—962).—The methods of estimating titanium, depending on the precipitation of titanic acid from solutions containing sulphurous and sulphuric acids, and the volumetric method involving reduction with zinc and subsequent titration with potassium permanganate, give low results. The methods in which the iron is reduced with sulphur dioxide or hydrogen sulphide, and the titanium precipitated with ammonia or by boiling with sodium or ammonium acetate and acetic acid, give high results when a large excess of iron is present.

A new method is now described which gives accurate results, and has been found useful for the analysis of rutile and iron ores. The silica is removed by means of hydrofluoric acid in presence of sulphuric acid. The residue is evaporated to dryness and fused with sodium carbonate and a little sodium nitrate in order to convert the iron and titanium into insoluble ferric oxide and sodium titanate, and afterwards extracted with hot water to remove the soluble phosphates, sulphates, and aluminates. The ferric oxide and sodium titanate are dissolved in hydrochloric acid, and the ferric chloride is extracted by means of ether. The remaining traces of iron are reduced with sulphur dioxide and the titanic acid is precipitated by boiling with acetic acid, and afterwards collected and converted into titanium oxide by ignition.

If the titanium is present only in small quantity, it can be estimated colorimetrically. The solution, after extraction with ether, is heated to expel dissolved ether. When cold it is transferred to a Nessler's tube and treated with hydrogen peroxide, diluted to a particular volume, and compared with standard solutions of titanic acid in hydrochloric acid which have been similarly treated with hydrogen peroxide.

Rosenheim and Schütte (Abstr., 1901, ii, 244) have described a yellowish-white compound obtained by the action of an ethereal solution of hydrochloric acid on titanium hydroxide. It has now been

found that this compound is colourless if the ether employed is free from peroxide. E. G.

Gravimetric Estimation of Vanadium as Silver Vanadate. PHILIP E. BROWNING and HOWARD E. PALMER (*Amer. J. Sci.*, 1910, [iv], **30**, 220—222).—Experiments made to determine the conditions under which vanadium can be estimated gravimetrically as silver vanadate show that the precipitate formed by the addition of silver nitrate to a neutral solution is of constant composition, corresponding with the meta-vanadate. From solutions acidified with acetic acid, a silver salt of variable composition is precipitated. H. M. D.

Application of Potassium Ferricyanide in Alkaline Solution to the Estimation of Vanadium and Chromium. HOWARD E. PALMER (*Amer. J. Sci.*, 1910, [iv], **30**, 141—145).—A continuation of the previous paper on this subject (this vol., ii, 546).

Estimation of Vanadium.—The vanadate (about 0·1 gram present as an ammonium salt) is acidified with hydrochloric acid and reduced to the blue compound by passing a current of sulphur dioxide. The solution is then boiled in a current of carbon dioxide to expel the last traces of the sulphur dioxide. When cold, a solution of potassium ferricyanide is added in quantity at least ten times that theoretically required, followed by 6 grams of potassium hydroxide. After diluting to 100—125 c.c., the vanadic acid is removed by adding solution of barium hydroxide, and the liquid is filtered through an asbestos filter. The filtrate and washings are then acidified with hydrochloric acid, and the ferrocyanide formed in the reaction is titrated with permanganate. Two mols. of ferrocyanide = two atoms of vanadium.

Estimation of Chromium.—The process worked out by Bollenbach and Luchmann (Abstr., 1909, ii, 187) gives good results if at least fifteen times the theoretical quantity of ferricyanide is used and a stronger potassium hydroxide solution is added. In this process the chromum is removed before the titration as barium chromate. After acidifying with hydrochloric acid, an excess of permanganate is added, and this is titrated in turn by means of $N/20$-ferrocyanide in presence of a trace of a ferric salt, the end point being indicated by the appearance of a green coloration.

Estimation of mixed Vanadium and Chromium.—About 0·2 gram of the mixed compounds, both in the higher state of oxidation, are dissolved, and the solution is divided into two equal portions. In one of these the salts are reduced by means of sulphur dioxide as directed, and a sufficient excess of potassium ferricyanide and potassium hydroxide is added. Both vanadate and chromate are then removed by means of barium hydroxide, and the filtrate is acidified with hydrochloric acid. The solution is then titrated with permanganate as in the case of chromium.

The second portion is titrated for vanadium only, as follows: To the solution, measuring about 100 c.c., are added 10—15 c.c. of glacial acetic acid and then hydrogen peroxide. On boiling, the chromium is reduced to oxide, whilst the vanadium is not affected. A solution of lead acetate is added, which causes a precipitate of lead vanadate,

which becomes more compact when the liquid is heated to boiling. The precipitate is collected on asbestos, washed thoroughly, and dissolved in aqueous potassium hydroxide. The lead is then removed by adding excess of sulphuric acid, and the vanadium reduced by passing a current of sulphur dioxide. After boiling in a current of carbon dioxide, the vanadium is titrated with permanganate.

The amount of permanganate required for the oxidation of the chromium is then found by difference. L. DE K.

The Separation of Antimony and Tin by Distillation. WILHELM PLATO (*Zeitsch. anorg. Chem.*, 1910, 68, 26—47).—Antimony may be completely separated from tin by distillation of its chloride, the tin being fixed by means of phosphoric acid. The boiling point of the mixture is best raised by the addition of sulphuric acid. A Jena glass Kjeldahl flask is used, provided with a rubber stopper, through which pass a thermometer, a tap-funnel with stem reaching nearly to the bottom of the flask and fitted with a side arm, and a gas delivery tube connected to a condenser. The lower end of the condenser is bent, and reaches to the bottom of the receiver. A second tube forms a reflux condenser for this receiver.

The substance containing tin and antimony, such as the mixture of sulphides, is dissolved in 6 c.c. of concentrated sulphuric acid, and transferred to the flask together with 7 c.c. of phosphoric acid, D 1·70, and, after cooling, 10 c.c. of hydrochloric acid are added through the tap-funnel. About 50 c.c. of hydrochloric acid are then placed in the receiver, and the apparatus is connected. During the first heating, carbon dioxide is led into the flask, and the reflux condenser is connected with a draught. When the temperature reaches 155—165°, it is kept constant by adding fuming hydrochloric acid at the rate of 50—60 drops a minute. The distillation lasts one and a-half hours, and the whole of the antimony is then contained in the receiver. It is estimated by any of the usual methods.

The tin remaining in the flask may now be distilled into a receiver containing hydrochloric acid. The tap-funnel is filled with a solution of bromine in fuming hydrochloric acid, and 6 c.c. of concentrated sulphuric acid are introduced into the flask. Instead of carbon dioxide, a current of sulphur dioxide is passed through the liquid during the distillation, and the temperature is kept constant at 180—190°. After an hour, all the tin is present in the receiver as tetrachloride. Sulphur dioxide is then removed by a current of carbon dioxide, the receiver being heated.

Antimony is best estimated as the trisulphide, and tin by precipitation as sulphide together with a mercury salt, in order to yield a precipitate which is readily filtered, finally igniting to stannic oxide.

When arsenic is also present, it is best to distil the solution in sulphuric acid so as to drive both arsenic and antimony over. After adding 5 grams of tartaric acid to the distillate, it is distilled in a current of carbon dioxide, when all the arsenic passes over. The separations may be combined by using a receiver, containing hydrochloric and tartaric acids, heated so that the arsenic distils over into a second receiver. Lead is obtained directly as sulphate on

diluting the residue in the distilling flask, and copper may then be estimated electrolytically in the filtrate. C. H. D.

Electric Combustion Furnace for Methane Estimation. J. August Fries (*J. Amer. Chem. Soc.*, 1910, **32**, 949—953).—A special combustion furnace has been devised for the estimation of the combustible gases, chiefly or wholly methane, excreted by cattle in the course of respiration calorimeter experiments. The quantity of air taken for analysis from the respiration calorimeter chamber amounts to 3·5 litres per minute. This volume passes through the combustion tube in which the combustible gases are oxidised, platinised kaolin serving as a catalyst.

The combustion tube is a copper tube of 20 mm. internal diameter and 3·35 metres long; the portion heated is protected by a nickel-plated brass tube which fits loosely over it. The outside box and supports for the tube are constructed of asbestos board, three-quarter inch thick. The resistance coils are wound on three quartz tubes of 37 mm. internal diameter and 70 cm. long. A full description of this furnace is given in the original.

This electric furnace is to be preferred to the gas furnace, as it gives a more uniform heat, can be easily regulated, and obviates the danger of the air supply of the respiration calorimeter becoming contaminated with combustible gases. E. G.

Condensation of Petroleum and its Distillates with Methylal and Sulphuric Acid. V. F. Herr (*Chem. Zeit.*, 1910, **34**, 893—894). —Nastukoff's formalin process for the estimation of the hydrocarbons in petroleum which form condensation products with this aldehyde (Abstr., 1904, i, 80) does not yield concordant results, and the product is partly soluble in chloroform. Methylal is a more sensitive reagent for the purpose; by it 0·05 vol. % of benzene can be detected, whereas formalin only indicates the presence of 5% of benzene.

The reaction with methylal depends largely on the temperature. A mixture of 5 grams of Baku spindle oil, D 0·900, and 10 grams of methylal, cooled by water, is treated with 10 c.c. of concentrated sulphuric acid in a fine stream; when cold the mixture is poured into 200 c.c. of water, and is neutralised with ammonium hydroxide, the precipitate is collected on several layers of filter-paper, dried at 115°, washed with water and light petroleum, and is again dried at 115°; the product is a brownish-black substance (C 75·86, H 10·4, S 6·98%), which is soluble in chlorobenzene; yield 7%. When the reaction is carried out without cooling, and the mixture is heated on the water-bath before being poured into water, the purified product is a dark brown powder (C 68·94, H 7·12, S 7·19%), which is insoluble in chlorobenzene and the usual solvents; yield 26%. A rapid volumetric modification of the process, which yields relative results, and is suitable for the detection of the adulteration of light oil with decolorised Surachany crude oil, and of benzine with cheap tar-oils, is the following: Two c.c. of the oil and 4 c.c. of methylal, dissolved in 10 c.c. of light petroleum, b. p. 50° (which does not react with methylal), are placed in a graduated stoppered cylinder, treated drop

by drop with 2 c.c. of sulphuric acid, and vigorously shaken for one minute; after half an hour, the volume of the precipitate, which has settled at the bottom of the cylinder, is read. C. S.

Assay of the Halogen Compounds of the United States Pharmacopœia with Special Reference to Thymol Iodide. ELIAS ELVOVE (*Amer. J. Pharm.*, 1910, **82**, 403—409).—It is considered desirable that a general process for the estimation of halogen compounds should be inserted in the United States Pharmacopœia, and for this purpose the method described by Wallis (Abstr., 1906, ii, 255) or that of Self (Abstr., 1907, ii, 657) is considered suitable. Thymol iodide is particularly difficult to decompose quantitatively (Gane and Webster, Abstr., 1909, ii, 613), but trials show that the following modification of Self's process gives good results. The iodide (0·1 to 0·5 gram) is mixed with ether (10 c.c.), *N*/2-sodium hydroxide in alcohol (20 c.c.), and zinc dust (2 grams), and boiled under a reflux apparatus during one hour. Glacial acetic acid (10 c.c.) and water (200 c.c.) are then added, and the mixture again boiled during one hour. The reflux apparatus is washed out into the flask, and the contents of the latter filtered and the filter washed with hot water (30 c.c.). To the filtrate a definite amount of *N*/10-silver nitrate solution is added, in excess of about 5 c.c. The mixture is boiled during ten minutes, 50 c.c. of 10% nitric acid added, and the whole again boiled during five minutes. The filtrate from this with the washings (30 c.c. of hot water) is cooled, and the excess of silver nitrate titrated by standard thiocyanate, using 5 c.c. of a 10% solution of iron alum as indicator. Chlorine in the compound can be determined by calculation from the weight of the silver precipitate. T. A. H.

The α-Naphtholsulphuric Reaction for Dextrose. LASZLÓ VON UDRÁNSZKY (*Zeitsch. physiol. Chem.*, 1910, **68**, 88—92. Compare Abstr., 1888, 863).—Concentrated sulphuric acid added to a solution of dextrose and α-naphthol produces a violet ring where the two liquids meet.

The green coloration observed by Goldschmiedt (this vol., ii, 555, 759) in testing urines is probably not due to glycuronic acid, but to nitrates or nitrites present in the urine. J. J. S.

A New Method for Estimating Sugar in Urine. K. A. HASSELBALCH and J. LINDHARD (*Biochem. Zeitsch.*, 1910, **27**, 273—295). —An alkaline solution of safranine and other dyes is decolorised by dextrose and other carbohydrates. For quantitative purposes equal parts of a solution of safranine (1 in 10,000) and potassium hydroxide (1 in 100) are mixed. Two c.c. of this mixture, or more if the quantity of sugar in the urine is large, are mixed with a known number of drops of a sugar solution, and the mixture is warmed on a water-bath. The amount of sugar is estimated by ascertaining the number of drops which are required just to decolorise the alkaline mixture, which can be standardised by a sugar solution. The authors claim that the method has the advantage over other methods in that a preliminary separation of proteins is unnecessary, and that the

reduction due to substances in the urine other than sugars is only about one-quarter of that found in the Bang-titration method. The authors also give the results of a large number of sugar estimations in normal and pathological urines. The reagents employed do not deteriorate on keeping. S. B. S.

New Reactions for Salicylic Acid. C. REICHARD (*Pharm. Zentr.-h.*, 1910, 51, 743—749).—Numerous new reactions for salicylic acid are communicated. Of the more characteristic tests, the following are the most important. A pinch of titanic acid is moistened with sulphuric acid and heated for a short time; it is not necessary to effect solution. A little salicylic acid is now added, and the whole set aside for a few hours. If now a drop of aqueous potassium hydroxide is allowed to come in contact with the mixture, a fine orange-red coloration will be noticed. Reversely, the test may be used for the detection of titanic acid.

A mixture of salicylic acid and copper sulphate moistened with hydrochloric acid when exposed to the air loses its green colour, but after some days a reddish-violet coloration appears, resembling the biuret reaction for albumin. A concentrated solution of potassium ferricyanide turns dark green when mixed with salicylic acid, and, on adding a drop of strong aqueous potassium hydroxide, the liquid turns a dark green bluish-black, which disappears on shaking; the colour then changes to a slightly green brownish-yellow. L. DE K.

A Source of Error in the Detection and Estimation of Salicylic Acid. HENRI PELLET (*Ann. Chim. anal.*, 1910, 15, 302—305).—Attention is drawn to the fact that salicylic acid is a normal constituent of many fruits, etc. When the presence of salicylic acid is detected in an article of food or in a beverage, it is necessary to estimate the quantity present in order to ascertain whether the sample contains added salicylic acid. The amount present naturally, for instance in wine, is about 0·001 gram per litre, whilst it is necessary to add from 0·040 to 0·060 gram per litre before the acid has an effective preservation action. The substance discovered by Backe (this vol., i, 225) may also be mistaken for salicylic acid. W. P. S.

Estimation of Salicylic Acid in Jams, etc. TH. VON FELLENBERG (*Zeitsch. Nahr. Genussm.*, 1910, 20, 63—70).—The process described is a modification of that proposed by Harry and Mummery (Abstr., 1905, ii, 426); this method is considered to be untrustworthy, owing to the fact that a portion of the salicylic acid volatilises during the distillation of the ether, that the lead precipitate occludes salicylic acid, that three extractions with ether are insufficient to remove all the salicylic acid, and that the latter is contaminated with fruit acids which interfere with the colorimetric estimation of the salicylic acid. The details of the modified process are as follows: Fifteen grams of the sample are mixed with 50 c.c. of warm water, the mixture is neutralised with *N*-sodium hydroxide solution, and treated with $10-a$ c.c. of sodium citrate solution, a being the quantity of *N*-sodium hydroxide solution required for the neutralisa-

tion. The sodium citrate solution is prepared by neutralising 35 grams of citric acid with sodium hydroxide, and diluting the solution to a volume of 500 c.c. The mixture is now treated successively with 10 c.c. of basic lead acetate solution, D 1·24, 10 c.c. of *N*-sodium hydroxide solution, 5 c.c. of *N*-hydrochloric acid, and 40 c.c. of saturated sodium chloride solution. The addition of these salts prevents salicylic acid being retained in the lead precipitate formed. The whole mass is now diluted to a volume of 100 c.c., filtered, and 100 c.c. of the filtrate are acidified with 3 c.c. of 20% hydrochloric acid and shaken out with five successive quantities of 50 c.c. of ether. The united ethereal extracts are then rendered alkaline by the addition of 10 c.c. of *N*-sodium hydroxide solution, and the ether is removed by distillation. The residual solution is diluted with water to a volume of 50 c.c., acidified with 7 c.c. of 20% hydrochloric acid, and a measured excess of *N*/50-bromine solution is added. (This solution is prepared by dissolving 0·57 gram of potassium bromate and 2 grams of potassium bromide in 1 litre of water). After the lapse of five minutes, 0·5 c.c. of 10% potassium iodide solution is added for every 10 c.c. of the bromine solution used, and the liberated iodine is titrated with *N*/50-thiosulphate solution. The bromine and thiosulphate solutions must be titrated against each other under the same conditions as to dilution, acidity, etc., as in the actual estimation. Each c.c. of *N*/50-thiosulphate solution corresponds with 0·00046 gram of salicylic acid. The reactions taking place in this method of titrating the salicylic acid are shown by the formulæ:

$$(1)\ OH{\cdot}C_6H_4{\cdot}CO_2H + 8Br = C_6H_2Br_3{\cdot}OBr + 4HBr + CO_2$$

and (2) $C_6H_2Br_3{\cdot}OBr + 2KI = C_6H_2Br_3{\cdot}OK + KBr + I_2$. The excess of bromine added is also titrated as iodine, and the difference in the quantities of thiosulphate solution used in the actual estimation and the blank titration gives the amount of salicylic acid present.

It was found by experiment that the process yields only 90% of the salicylic acid actually present, and that jams contain substances which yield bromine-additive compounds, the quantity of these substances, expressed as salicylic acid, being about 0·05 gram per kilogram of jam. The apparent quantity of salicylic acid, S, in the sample is found from the equation: $S = 0{\cdot}046 \times T \times a$, where T is the titre of the thiosulphate solution, and a the quantity of thiosulphate solution used for 10 grams of the sample. The actual quantity, x, is obtained from the equation: $x = S - 0{\cdot}05 + 0{\cdot}1(S - 0{\cdot}05)$. The limit of error of the process is $\pm 0{\cdot}001$%. **W. P. S.**

Extraction Apparatus. GEORGE S. WALPOLE (*Chem. News*, 1910, **102**, 129—130).—A modified Soxhlet apparatus is described in which there are no corks, rubber stoppers, or ground-in joints. The extraction flask is provided with a flange in which the outer part of the extraction part of the apparatus rests, mercury being placed in this flange so as to form a mercury seal. An inner tube is placed in the extraction portion of the apparatus, and in this is fitttd a tube for holding the extraction thimble or cartridge; the lower part of the latter tube is provided with a siphon tube as in the Soxhlet apparatus. The condenser is attached by means of a blown-in joint to the top of

the outer tube. The extraction thimble may be dispensed with if desired, and the material to be extracted packed in the inner tube itself. W. P. S.

Fat Extraction Apparatus. WILLIAM CLACHER (*Analyst*, 1910, 35, 349).—The apparatus consists of a short glass tube, the lower end of which is closed by a linen cap; the substance to be extracted is filled into this tube, which is then suspended, open end upwards, in a wide-necked flask by means of threads. The flask contains a suitable solvent, such as ether, and is placed on a water-bath. The vapour from the boiling solvent is condensed on a test-tube inserted through the cork closing the flask, and the condensed liquid drops into the extraction tube and percolates the contents. The test-tube is provided with a supply of cold water, and a small opening in the cork of the flask prevents excessive pressure of vapour in the latter. A small hole in the side of the extraction tube near the top allows the condensed liquid to pass from the tube into the flask should the rate of condensation exceed the speed at which the solvent percolates the substance.

W. P. S.

Detection and Estimation of "Saccharin" in Foods containing Fats, Starch, and Proteins. MASSIMO TORTELLI and E. PIAZZA (*Ann. Falsif.*, 1910, 3, 313—320).—The following procedure is recommended for separating "saccharin" from foods, and for removing fatty substances extracted along with the "saccharin." The sample is mixed with sand and a small quantity of calcium hydroxide (liquid foods are evaporated to dryness after the addition of the sand and calcium hydroxide), and the mixture is extracted several successive times with boiling alcohol, a quantity of saturated sodium chloride solution being added with each quantity of alcohol. The united alcoholic extracts are then filtered, and the filter is washed with a hot mixture of alcohol and sodium chloride solution. The filtrate is evaporated to a volume of about 70 c.c., 15 c.c. of saturated sodium chloride solution are added, and the mixture is shaken several times with light petroleum to remove fatty substances. The residual solution is next heated to expel all the remaining alcohol, then acidified with sulphuric acid, and the "saccharin" is extracted with a mixture consisting of equal volumes of ether and light petroleum. On evaporating the separated solvent, the "saccharin" is obtained as a crystalline residue. A substance similar to "saccharin" is sometimes present in foods, namely, "dulcin" or "sucrol" (*p*-phenetolecarbamide). It is extracted from the food along with "saccharin" as described above by means of alcohol, but it is only slightly soluble in the light petroleum-ether mixture, and is quite insoluble in light petroleum; it is entirely soluble in ether alone. "Saccharin," m. p. 223°, may be distinguished from "dulcin," m. p. 173°, from the fact that the former contains sulphur. "Dulcin" gives a faint violet coloration when heated with mercuric nitrate solution; this coloration becomes more intense on the addition of a trace of lead peroxide. W. P. S.

Bitter Wines and the Acrylic Fermentation of Glycerol. E. VOISENET (*Compt. rend.*, 1910, **151**, 518—520. Compare this vol., ii, 738).—Denigès' reaction (Abstr., 1909, ii, 272, 273) may be employed to recognise the presence of acraldehyde in bitter wines, the distillate being treated successively with bromine, baryta water, and carbon dioxide to convert the aldehyde into dihydroxyacetone.

The amount of acraldehyde found gives no indication of the amount originally formed, since a portion undergoes conversion into acrylic acid and resinous products, the latter giving rise to the characteristic bitterness. W. O. W.

The [French] Official Method for Titrating Pyramidone. PAUL LEMAIRE (*Ann. Chim. anal.*, 1910, **15**, 307—308).—The author draws attention to an error in the directions prescribed by the French Codex for the titration of pyramidone; 5 grams of the sample, instead of 0·5 gram, should require not less than 20 c.c. of *N*-acid for neutralisation. He also points out that the titration, using methyl-orange as indicator, yields results which vary slightly according to the dilution, temperature of the solution, and quantity of methyl-orange added.
W. P. S.

Estimation of Creatinine. PETER RONA (*Biochem. Zeitsch.*, 1910, **27**, 348).—Folin's colorimetric method can be advantageously applied to meat-essences, urine, etc., if the pigment be first removed by ferric hydroxide, which does not adsorb the creatinine. S. B. S.

Detection of Ornithine in the Cleavage Products of Proteins. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1910, **68**, 160—164. Compare Abstr., 1909, i, 542).—In the absence of lysine, ornithine can, after the removal of histidine and arginine, be isolated readily as picrate, aurichloride, or most readily as its benzoyl derivative. In the presence of lysine, it is most readily isolated as the picrate, as this is much more readily soluble in water, or especially in methyl alcohol, than lysine picrate.

d-Ornithine monopicrate (Schulze and Winterstein, Abstr., 1902, i, 231) has m. p. 203—204°, and contains $1H_2O$. *dl*-Ornithine monopicrate (Fischer and Raske, Abstr., 1905, i, 863; Riesser, Abstr., 1907, i, 78) forms large, triclinic crystals and is anhydrous (Riesser gives $1·5H_2O$).

A *dipicrate*, $C_5H_{12}O_2N_2,2C_6H_3O_7N_3$, has m. p. 195°, and does not appear to be identical with the products described by Fischer and Raske and by Riesser, and is formed to a slight extent when the monopicrate is recrystallised.

dl-*Ornithine dipicrolonate*, $C_5H_{12}O_2N_2,2C_{10}H_8O_5N_4$, has m. p. 235—236°.

One hundred c.c. of methyl alcohol dissolve 4·2—4·5 grams of *dl*-ornithine dipicrate and 2·5—3 grams of *dl*-monopicrate, but only 0·3—0·4 gram of *d*-ornithine monopicrate.

The process of separation from lysine works best with the inactive ornithine, and when *r*-ornithine is present, it is advisable to racemise by means of concentrated sulphuric acid before carrying out the separation. J. J. S.

Reactions of Alkaloids with Hydrogen Peroxide. ED. SHAER (*Arch. Pharm.*, 1910, **248**, 458—462).—A description is given of the colour reactions of many of the alkaloids with a reagent made by mixing 1 volume of Merck's 30% "perhydrol" with 10 volumes of pure sulphuric acid. As a rule, the colour reactions are less characteristic than others already known. Quinine, however, produces, even in minute quantities, an intense citron-yellow to canary-yellow coloration. Nicotine and hydrastine produce intense chocolate-red colorations. C. S.

The Volumetric Estimation of Hydroferro- and Hydroferricyanic Acids. ERICH MÜLLER and OTTO DIEFENTHÄLER (*Zeitsch. anorg. Chem.*, 1910, **67**, 418—436. Compare Mecklenburgh, this vol., ii, 761).—The titration of ferrocyanides with permanganate, the accuracy of which has been called in question, gives good results when carried out by using a solution containing about 1 gram of the ferrocyanide in 150—200 c.c. of water, adding 20 c.c. of sulphuric acid (1 : 4), and titrating with $N/20$-potassium permanganate until the colour becomes yellowish-red. Ferricyanides are estimated in the same way after reduction with ferrous sulphate in alkaline solution.

The estimation of hydroferricyanic acid by addition of an excess of iodine and titration with thiosulphate in alkali hydrogen carbonate solution is inaccurate, owing to the action of the carbonate on iodine (Foerster and Gyr, Abstr., 1903, ii, 209), and the use of arsenious acid does not give better results.

Ferricyanides may be accurately titrated in neutral solution, containing about 0·7 gram in 50 c.c. of water, by adding 3 grams of potassium iodide and 1·5 grams of pure zinc sulphate, and titrating with thiosulphate and starch immediately after shaking. C. H. D.

Chemical Tests for Blood. PHILIP A. KOBER, W. G. LYLE, and J. T. MARSHALL (*J. Biol. Chem.*, 1910, **8**, 95).—Most observers recognise that whilst substances other than blood give a positive reaction with the guaiacum and similar tests, a negative result is a proof of its absence. This must be corrected, for solutions of tannic acid or extracts of tea or coffee prevent the occurrence of the reaction when a small amount of blood is present in the gastric contents. In using the Ewald-Boas test meal, water and not tea should therefore be given. W. D. H.

A New Colorimeter and its Application to the Estimation of the Colouring Matter of Blood, Iron, Indican, and Creatinine. WILHELM AUTENRIETH and JOHANN KOENIGSBERGER (*Münch. med. Woch.*, 1910, No. 19, 1—10).—The colorimeter which is described and figured is chiefly designed for measurements in physiological chemistry. Its advantages are that measurements are made by displacement of the comparison vessel, so that no dilutions are necessary; the vessels have parallel walls, and are thus more satisfactory than circular tubes, and, further, a very accurate comparison of the two colours is rendered possible by the use of a Helmholtz double plate, which abolishes the line of separation. In

each case the comparison solutions employed are stable and readily reproducible.

The determination of the proportion of colouring matter and of iron in blood, and of indican and creatinine in urine, by means of the colorimeter is described in detail, the standard methods described by previous observers being used in each case. In the course of the experiments it was found that the amount of creatinine secreted in the urine in one day varied from 1·7 to 2·3 grams. G. S.

Clinical Reagent for Urobilin, Urobilinogen, and Blood. ALBERT FLORENCE (*J. Pharm. Chim.*, 1910, [vii], 2, 160).—The development of colour, which occurs naturally in hæmapheic urines on keeping is expedited by mixing from 2 to 3 c.c. of the urine with twice its volume of a solution of zinc acetate (7·5 grams) in a mixture of 50 grams each of pyridine, alcohol, and chloroform. On shaking and setting aside, the lower layer remains colourless if no pigments are present, fluoresces green if urobilin is present, gradually fluoresces green for urobilinogen, is greenish and eventually fluorescent for biliverdin, and is rose- or cherry-red if blood occurs in the urine. The intensity of the colour may be used to estimate approximately the quantity of pigment present. The solutions show well marked spectrum bands. T. A. H.

Estimation of Hæmapheic Pigments. ALBERT FLORENCE (*J. Pharm. Chim.*, 1910, [vii], 2, 161—163).—The urine is placed in a cylindrical bromine tube, one-fifth of its volume of acetone added and then granular ammonium sulphate to saturation, and the mixture shaken. The acetone dissolves the pigments, and separates as a definite layer, from which the aqueous liquor may be drawn off. The acetone solution is then dried by means of granular ammonium sulphate, and on evaporation in a tared vessel leaves, as a residue, the "total hæmapheic pigments." From this, chloroform removes urobilin, leaving a red acid deliquescent pigment, soluble in alcohol, which does not give a band spectrum and does not fluoresce with zinc salts.

T. A. H.

Detection of Blood with Guaiacum Resin with the Aid of Sodium Perborate. BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Chem. Zeit.*, 1910, **34**, 814—815).—To 5 c.c. of the liquid to be examined (urine, for instance) are added a few drops of cold saturated, freshly prepared tincture of guaiacum, and then 1 c.c. of powdered sodium perborate, followed by 10 c.c. of 30% acetic acid. After shaking, the test-tube is sharply inclined, and a little alcohol is carefully poured over the surface of the liquid. If blood is present, a blue or bluish-green coloration will be noticed at the place of contact within five minutes.

Guaiacum resin which has turned greenish or bluish-green either on the surface or throughout the mass should not be used. L. DE K.

A Delicate Reaction for Glue. EUGEN SCHMIDT (*Chem. Zeit.*, 1910, **34**, 839).—The reagent consists of a solution of 3 grams of

ammonium molybdate in 250 c.c. of water and 25 c.c. of nitric acid, D 1·2.

This reagent is particularly suited for the detection of glue in fabrics. The sample is boiled with water, the solution is concentrated on the water-bath, and then treated with the reagent, which will cause a heavy white precipitate. Other substances used in dressing fabrics, such as gum arabic, decoction of linseed, etc., only give a turbidity, but no characteristic precipitate. L. DE K.

Urine Colorations. C. J. REICHARD (*Pharm. Zeit.*, 1910, **55**, 638).—When applying the nitric acid boiling test to urines, the author prefers using a nitric acid, D 1·12. At first this is added until the urine has a decided acid reaction, and then during the boiling more acid is added until the coloration no longer increases. If acid of greater strength is used, the coloration is in danger of being destroyed.

The colour reaction is due, not only to the action of the acid on the existing colouring matters of the urine, but also to carbohydrates and mucin if present. The colouring matters formed, including humin substances, may be for the greater part removed by shaking with amyl alcohol. L. DE K.

A Simple Estimation of Trypsin and the Law of Trypsin Fermentation. ALEXANDER PALLADIN (*Pflüger's Archiv*, 1910, **134**, 337—364).—A protein such as fibrin or glue is dyed before immersion in the trypsin solution. As fermentation proceeds, the solution becomes coloured proportionately to the amount of protein dissolved, and an estimation of the amount of trypsin present is effected by colorimetric comparison with the result of a similar fermentation by a known amount of trypsin in the same time. The dyeing of the protein is best effected with "spirit blue, blue shade" (Farbenfabriken vorm. F. Bayer & Co.). The method has also been employed to determine the law according to which trypsin fermentation proceeds, as this has been the subject of conflicting statements. It has been found that in the case of the fermentation of a solid protein, or of glue, when care is taken that the surface of contact of solid and solution always remains the same size, the amount fermented is nearly proportional to the cube-root of the square of the amount of ferment present. When the protein is powdered, or enclosed in Mett tubes, the amount fermented is more nearly proportional to the square root of the amount of ferment in the solution, whilst when the protein is in solution the amount hydrolysed is simply proportional to the quantity of ferment present. The latter result confirms that of Gross (compare Abstr., 1908, i, 234), and was obtained by his method. R. V. S.

General and Physical Chemistry.

Solutions. I. Relations between Density and Refractive Index in Binary Mixtures. F. Schwers (*Bull. Soc. chim.*, 1910, [iv], 7, 875—882).—Pulfrich's formula, $(D - D_v)/D = a(N - N_v)/N$, expressing the relationship between change of volume and change in refractive index from the calculated values for any binary mixture of liquids, does not admit of an absolute comparison between the two changes, since in devising the formula Pulfrich introduced the density value in arriving at the refractive index contraction, N_v. The author suggests instead the relation: $C_n = AC_v$, where $C_n = 100(n - n_v)/n$, n being the observed refractive index of the mixture and n_v the calculated value, and $C_v = 100(D - D_v)D$, D being the observed specific gravity and D_v the calculated value. The value of A has been determined for mixtures of water with alcohol, acids, aldehydes, ketones, glycols, hydroxy-acids, esters, ethers, amines, cyclic compounds, etc., and from the results obtained the following conclusions are drawn. The value of A for a mixture of two given liquids is independent of (1) the concentration of either constituent, (2) the wave-length of the light used, and (3) to a certain extent of the temperature of observation. It is specific for each mixture, and its magnitude is dependent on the molecular volume and structure of each constituent.

These observations lend no support to the "hydrate" theory of solution, since if "hydrates" were formed it is inconceivable that A would be independent of the concentration of each constituent in a given binary mixture.

When a substance undergoes change in volume (by compression, polymerisation, or fusion), the change in refractive index exhibits a relation to the change in volume, which is peculiar to each substance and depends on its constitution. T. A. H.

Fluorescence and Band Spectra of Oxygen. Walter Steubing (*Ann. Physik*, 1910, [iv], 33, 553—584).—It has been found that oxygen exhibits three banded emission spectra, one of which lies in the region extending from the red to the greenish-yellow rays, whilst the others are in the ultra-violet. Detailed observations relating to the three spectra are recorded. The first ultra-violet spectrum, which has usually been attributed to water-vapour by previous observers, is shown to be characteristic of oxygen. The bands of this spectrum, in the neighbourhood of $185\mu\mu$, were repeatedly obtained under conditions which seemed to ensure the absence of water vapour. These conditions were such that the strongest hydrogen lines are not visible, and the author concludes that the first ultra-violet spectrum exhibited by tubes containing oxygen cannot be due to water vapour.

The experimental data are discussed from the point of view of Stark's electron theory. H. M. D.

Dispersion of Light by Potassium Vapour. P. V. BEVAN (*Proc. Roy. Soc.*, 1910, **84**, *A*, 209—225).—In continuation of previous experiments (compare Abstr., 1909, ii, 783; this vol., ii, 87) on the dispersion produced by potassium vapour, quantitative measurements have now been made for different wave-lengths. The observed deviations extend over the whole of the visible spectrum and for a considerable distance in the ultra-violet. Strong absorption takes place at the lines of the principal series, and anomalous dispersion is found in the neighbourhood of these lines. This phenomenon has been investigated for seven of the pairs forming the principal series lines. As the pairs in this series get closer together with diminishing wave-length, the dispersion effects can only be seen outside the lines forming a pair, and a lack of symmetry in the dispersion curves is found which corresponds with the different intensities of the lines forming the pair. The quantitative data are discussed in reference to Sellmeier's theory.

In regard to the natural periods which correspond with the series lines, it is suggested that these are not due to the atom itself, but to differentiated forms of the atom exhibiting real differences in physical properties. H. M. D.

Series Spectrum of Mercury. S. R. MILNER (*Phil. Mag.*, 1910, [vi], **20**, 636—642).—It has been found that the photographic records of the spectrum of the mercury arc in a vacuum show no trace of the continuous back-ground even when the time of exposure is more than fifty times as long as the normal exposure suitable for registration in the case of the mercury arc in air. These records show a large number of lines which have not been observed previously.

The wave-lengths of the lines of the principal series down to $m=16$ in Rydberg's formula, and of the diffuse and sharp series down to $m=16$ and $m=14$ respectively, have been measured. The data are utilised to show the accuracy of Rydberg's empirical law, according to which the difference of the frequency of the convergence limit of the principal series and that of the common limit of the sharp and diffuse series is equal to the frequency of the first line of the sharp series.

The agreement is such as to indicate the absolute accuracy of this law. H. M. D.

Influence of Pressure on the Absorption of Ultra-red Radiation by Gases. EVA VON BAHR (*Ann. Physik*, 1910, [iv], **33**, 585—597).—In continuation of previous measurements (Abstr., 1909, ii, 630) of the dependence of the ultra-red absorption on the pressure, experiments have been made with sulphur dioxide, hydrogen chloride, nitrogen peroxide, ozone, benzene, and methyl alcohol. As in the case of the gases examined previously, the absorption of the first four substances increases as the total pressure on the gas is raised, and tends towards a constant maximum value. For benzene and methyl alcohol, on the other hand, the absorption is independent of the pressure between 5 and 760 mm. The collected data indicate that, in general, the pressure at which maximum absorption is reached diminishes as the size of the molecules of the gas increases.

Experiments with nitrous oxide show that a change of pressure, not only influences the quantity of the absorbed radiation, but also brings about a change in the character of the absorbed rays. This variation in the nature of the absorbed radiation is inconsiderable, except at lower pressures. H. M. D.

A New Radiant Emission from the Spark. ROBERT W. WOOD (*Phil. Mag.*, 1910, [vi], 20, 707—712).—When a condenser spark passes between aluminium electrodes screened by a metal strip, although nothing is visible to the eye, a photograph taken with a quartz lens shows that the air round the spark is glowing with ultra-violet light for a very short distance. This was shown not to be due to fluorescence of the air caused by the absorption of Schumann waves, or to scattering of the light of the spark by air or dust. The light given out by the emission is embraced between the wave-lengths of 300 to 310, and its spectrum consists of two broad bands, one very strong, the other weaker, identical with the "water bands" of the oxyhydrogen flame. In addition are three lines at 3576, 3537, and 3369, identical with those attributed by Eder and Valenta to nitrogen in the spectrogram of the spark between wet carbon poles. No difference was observed whether the spark took place in dry or moist air, but in oxygen there was practically no emission, whilst in nitrogen it was much brighter and extended a greater distance. No substance has been found transparent to the emission itself. A jet of oxygen killed the emission, but in a jet of nitrogen the emission shot out much further and was of greater intensity. The emission appears to be shot out with very high velocity, for it is not affected by air currents. The new emission appears of great importance in connexion with the origin of the so-called "water-bands," and it is possible it may be identical with the "Entladungsstrahlen." F. S.

Rotatory Power of Tartaric and Malic Acids in Presence of Ammonium Molybdate and Sodium Phosphate. G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 130—138).—Seeking an explanation of the phenomena observed in connexion with the precipitation of ammonium phosphomolybdate in the presence of organic acids (this vol., ii, 804), the author has repeated and extended the work of Gernez (Abstr., 1889, 859, 1147), more especially in order to obtain indications as to whether the phosphate radicle enters into the organic complex. He confirms the results of Gernez as regards the rotatory power of tartaric acid in the presence of ammonium molybdate. Rise of temperature affects the rotatory power differently at different concentrations. The concentrations at which a decrease is observed are those at which a precipitation of phosphomolybdate can be effected. Sodium phosphate does not affect the rotatory power of tartaric acid to any marked extent, its influence being in fact no greater than that of sodium or ammonium chlorides. The action of sodium phosphate and ammonium molybdate together is similar to that of the latter substance alone, so that it is probable that the complex substances in solution involve only the acid and the molybdate. The results obtained with malic acid were similar. The author finds reason to doubt the state-

ments of previous workers as to the composition of the complex compounds present in these solutions. R. V. S.

Action of Quinones and their Sulphonic Derivatives on Photographic Images from Silver Salts. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE and ALPHONSE SEYEWETZ (*Compt. rend.*, 1910, **151**, 616—618).—*p*-Benzoquinone and its sulphonic derivative act as "reducing" agents in acid solution towards the negative photographic image. A solution containing 2% of *p*-benzoquinone and 0·5% of sulphuric acid is recommended for use in photography. This bleaches the opaque portions of the image more rapidly than the half tones. The reaction is explained by the equation:

$$C_6H_4O_2 + H_2SO_4 + 2Ag = C_6H_4(OH)_2 + Ag_2SO_4.$$

In the presence of an alkali chloride or bromide, however, *p*-benzoquinone produces strong intensification. The effect is less marked in the case of the sulphonic derivative. The solution recommended contains 0·5% of *p*-benzoquinone and 2·5% of potassium bromide. The reaction is represented as: $2C_6H_4O_2 + 2KBr + 2Ag + H_2O = C_6H_4(OK)_2 + C_6H_4(OH)_2 + Ag_2OBr_2$. W. O. W.

Temperature-coefficient of the Bleaching of Colouring Matters in the Visible Spectrum. B. SCHWEZOFF (*Zeitsch. Photochem.*, 1910, **9**, 65—70).—The influence of temperature on the rate of bleaching of cyanine, pinachrom, pinaverdol, and pinacyanol when exposed to light of known wave-length has been investigated. For a rise of 10° the increase in the rate of bleaching was found to vary from 1·036 to 1·084. These temperature-coefficients are the smallest which have yet been observed in connexion with photochemical changes. H. M. D.

Acceleration of the Bleaching of Colouring Matters by Aromatic Compounds. GOTTFRIED KÜMMELL (*Zeitsch. Photochem.*, 1910, **9**, 54—60).—The increased sensitiveness of colouring matters towards light in presence of certain aromatic compounds has been measured by means of Vogel's actinometer, using specially prepared chromate paper as a comparison standard. Observations were made on cyanine, methylene-blue, and erythrosin, the substances added being anethole, eugenol, *iso*eugenol, safrole, *iso*safrole, propenylphenol, and vinylanisole. To obtain comparable results, these were added in such quantity that the molar concentration of the sensitiser in the exposed collodion or gelatin film was in all cases twenty-five times as large as that of the colouring matter. From the tabulated results it is found that safrole and *iso*safrole lower the light sensitiveness of all three colouring matters. The other five substances accelerate in general the rate of bleaching, and the sensitising influence of the members of the group increases as the molecular weight decreases.

Experiments are described in support of the view that the bleaching is due to an oxidation process, and that the active substances accelerate the bleaching by acting as oxygen carriers. H. M. D.

The Probability Variations in the Distribution of α-Particles. ERNEST RUTHERFORD and HANS GEIGER [with a note by H. BATEMAN] (*Phil. Mag.*, 1910, [vi], 20, 698—707).—The object of the experiments was to see whether the rate of emission of α-particles was governed by the laws of probability, or whether the expulsion of one α-particle might not precipitate the disintegration of a neighbouring atom. The scintillations from the α-particles of a polonium source were observed by eye, and recorded on a chronograph tape by closing an electric circuit by hand at the instant of each scintillation. Two thousand scintillations a day were counted for five days, and the chronograph records examined. The differences between the number of scintillations observed, in successive one-eighth, one-quarter, and one minute intervals respectively, and the true average number (total number divided by total number of intervals) were compared with the expression deduced by Bateman from the theory of probability. If x be the true average number of particles observed in any interval, the probability that n α-particles are observed in the same interval is $\frac{x^n}{n!}\epsilon^{-x}$. The agreement between theory and experiment was found to be practically perfect, especially for the one-eighth minute intervals, and there is no evidence of greater variations than would be expected from a random distribution. F. S.

Rate of Emission of α-Particles from Uranium and its Products. J. N. BROWN (*Proc. Roy. Soc.*, 1910, *A*, 84, 151—154).—The number of α-particles emitted from pitchblende films of known weight per unit area has been determined by the scintillations produced in zinc sulphide. For thin enough films the number was proportional to the thickness, so that the total number emitted per gram per second could be calculated. The percentage of uranium in the pitchblende was determined. Per gram of uranium in the pitchblende the number emitted per second was $7{\cdot}36 \times 10^4$, in fair agreement with the number, $9{\cdot}25 \times 10^4$, calculated from Rutherford's value for radium. F. S.

The Number of α-Particles Emitted by Uranium and Thorium and by Uranium Minerals. HANS GEIGER and ERNEST RUTHERFORD (*Phil. Mag.*, 1910, [vi], 20, 691—698).—The number of α-particles emitted per second from one gram of uranium, calculated from the number emitted by radium and the ratio between uranium and radium in minerals, is 11,600, if each uranium atom emits one α-particle. On Boltwood's view (Abstr., 1908, ii, 454) that two α-particles per atom are emitted by uranium, and one from each of the subsequent α-ray products, the calculated number of α-particles emitted per second from an old mineral containing 1 gram of uranium is 96,700. The number has been experimentally determined by counting the scintillations produced on a zinc sulphide screen from very thin films of material. The scintillations from uranium are much fainter and more difficult to count than from the uranium minerals and from thorium. Films of pure uranoso-uranic oxide, selected Joachimsthal uraninite, and thorium oxide, five weeks old, from thorite, prepared by Boltwood, were employed. The number of α-particles per second per

gram of uranium or thorium were for these three preparations 23,700, 96,000, and 27,000 respectively. These represent the mean values, corrected for defects of the screen, escape of emanation from the uraninite, and decay of radio-thorium in the thorium oxide. These experiments confirm the view that uranium alone gives two α-particles, all its products giving only one per atom disintegrating. The agreement between the calculated and experimental numbers is closer than could be expected. It was observed that the scintillations from ionium were as bright as, if not brighter than, those from uranium, showing that the range of the α-particle from the latter is not greater than that of ionium (2·8 cm. of air), which is the lowest hitherto measured. A preliminary measurement of the range of the uranium α-particle gave 2·7 cm. F. S.

The Scattering of Homogeneous β-Rays and the Number of Electrons in an Atom. J. ARNOLD CROWTHER (*Proc. Roy. Soc.*, 1910, *A*, **84**, 226—247).—The fact that β-rays are scattered in a thickness of material far too small to effect the velocity of the rays renders experiments on scattering more simple theoretically than those on absorption. The results are interpreted of the theory of J. J. Thomson (*Camb. Phil. Soc. Proc.*, 1910, **15**, v), which is borne out in all points. Homogeneous β-rays from a radium source, produced in the manner previously described (compare this vol., ii, 672), are scattered by screens of various materials and thickness, and, by means of stops of various sizes, the scattered rays are confined to a known angle, and pass into an ionisation chamber so shaped that the paths of all rays through it are similar. The following results deduced from the theory were experimentally established: (1) for rays of given velocity and cone of given angle the intensity of the radiation, I, varies with the thickness, t, of material traversed according to the formula: $I/I_0 = 1 - e^{-k/t}$, where k is a constant; (2) $\phi/\sqrt{t_m} =$ constant, where t_m is the thickness necessary to cut down to one-half the radiation through a stop of angle ϕ; (3) $mv^2/\sqrt{t_m} =$ constant, where mv^2, twice the kinetic energy of the rays, is obtained from the magnetic deflexion. In addition, the results lend themselves to a calculation of the number of electrons in an atom, which is found to be three times the atomic weight for all atoms examined on the assumption that the positive electricity within the atom is not in an electronic condition, but uniformly distributed. An important experiment showed that homogeneous β-rays, when passed through only 0·001 cm. of platinum, are completely scattered, and are then absorbed by aluminium exponentially, whereas the absorption in aluminium alone is quite different, the curve having two inflexions in opposite directions, making the middle part nearly linear, as Wilson found. The view is taken that completely scattered homogeneous β-radiation is exponentially absorbed. F S.

Influence of the Temperature on the Change of Radioactive Substances. II. HEINRICH W. SCHMIDT and PAUL CERMACK (*Physikal. Zeitsch.*, 1910, **11**, 793—800. Compare Abstr., 1909, ii, 9).—The changes in β-rays from a quartz tube containing radium during

and after heating in a platinum-foil furnace at 1200° to 1300° have been exhaustively examined, and, amid much irregular variation, certain generalities have transpired. The γ-rays throughout in all the experiments show absolutely no definite change in intensity, while the β-rays, on heating the tube, suddenly increase to a maximum, remain constant during the heating (usually one-half to one hour), then, on cooling, very rapidly and steadily decrease to the value before heating, then increase in three hours to the value during heating, and finally, after many days, return to the value before heating. These results are attributed to (1) the gasification of the products radium-*A*, -*B*, and -*C* by the heating, whereby the absorption of β-rays, which takes place in the radium itself when these products are formed within it, no longer occurs; (2) the sudden adsorption into the mass of the radium again of these products on cooling; (3) the formation in three hours of a new set of products on the walls of the tube and not within the radium, due to the complete expulsion of emanation from the radium during heating; (4) the decay of this emanation with the four-day half-period, and the re-growth of fresh emanation and products within the radium as initially. All the quartz tubes after repeated heatings became porous, and allowed emanation to escape, but some tubes lasted far better than others. The β-rays of uranium-*X* were also examined similarly to those of radium, but apart from initial changes, due to the heat altering the distribution of the substance, no definite changes occurred. The conclusion is arrived at that none of the experiments prove any direct influence of temperature on the rate of transformation of a radioactive substance. F. S.

The Consequences of the Corpuscular Hypothesis of the γ-and *X*-Rays, and the Range of β-Rays. WILLIAM H. BRAGG (*Phil. Mag.*, 1910, [vi], 20, 385—417).—The paper reviews exhaustively the present state of knowledge of the ionisation, penetration, reflexion, scattering, transformation, etc., of cathode-, *X*-, α-, β-, and γ-rays from the point of view of the "corpuscular" or "entity" hypothesis, which recognises that each type of radiation consists of individual entities, to be followed, each by itself, from its origin through all its changes of direction and sometimes changes of form (conversion of cathode- into *X*-rays, of γ- into β-rays) until its gradually diminishing energy becomes too small to be detected. A method is described of determining the average range of β-rays in various substances, defined as the average weight of substance crossed by the β-ray, when its zig-zag path is straightened out, before it disappears. It is deduced theoretically that the relative ionisations inside similar vessels of different materials, thick enough in the walls to prevent β-rays penetrating them, exposed to a constant stream of γ-rays, gives the relative average ranges of the β-rays in the metals. Results so obtained by H. L. Porter show the greatest range in lead and the least in card. The greater apparent absorption in lead than in other substances is due to the more zig-zag character of the path of the β-ray in lead, the total length of path (in weight units) being actually the greatest in lead. The view is strongly upheld that γ- and *X*-rays do not ionise gases directly at all, but only through first being transformed into

β- or cathode-radiation. The chief evidence against the corpuscular theory is from the work of Barkla on polarisation of X-rays, which, however, is considered a much more simple phenomenon than the polarisation of light, and one not necessarily calling for a wave-motion explanation. The attempt is made to explain the homogeneous secondary X-radiation of Barkla by a double transformation, first of primary X-rays into cathode-rays, and, secondly, the reconversion of the latter into "secondary" X-rays, the existence of a critical speed being assumed, which it is necessary for a cathode-ray falling on an atom to possess in order to produce an X-ray. F. S.

Typical Cases of Ionisation by X-Rays. CHARLES G. BARKLA (*Phil. Mag.*, 1910, [vi], **20**, 370—379).—The relative ionisations in air, carbon dioxide, and ethyl bromide produced by the homogeneous secondary X-rays from twelve elements with atomic weights lying between iron and antimony have been studied. The iron radiation was seventy times more easily absorbed than that from antimony, and throughout the whole range of penetrating power the ionisation in carbon dioxide was proportional to that in air, being about 1·4 times greater.

Similar results hold for other gases less dense than carbon dioxide. For ethyl bromide and air the proportionality held for radiations not more penetrating than the bromine radiation. For more penetrating secondary X-rays the relative ionisation of ethyl bromide rises suddenly to over three times its previous value, and then more slowly with increasing penetrating power to between five and six times. These results are similar to those previously found for the absorption of the radiations. Similar variations occur in the ionisations in vapours of methyl iodide, stannous chloride, and selenium chloride at the particular penetrating power characteristic of iodine, tin, and selenium, while carbon, hydrogen, and chlorine give no characteristic secondary X-radiation. No anomalous cases of X-ray ionisation have been observed. The penetrating power of the characteristic secondary X-radiation emitted by the constituent elements of the gas determine the way in which the ionisation depends on the penetrating power of the ionising radiation. F. S.

The Accumulation of Helium in Geological Time. IV. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, *A*, **84**, 194—196. Compare this vol., ii, 175).—Several examples of Archean rocks show a higher ratio of helium to radioactive matter than thorianite. The minimum age indicated by the helium ratio for sphenes from Archean rocks is about 700 million years. A sphene from the recent volcanic rocks of the Laacher Sea showed a helium ratio at least two thousand times less. An explanation for the anomalous case of beryl which contains helium out of all proportion to its radioactive content, due to Boltwood, is that in the crystallisation of the beryl one of the longer-lived products of disintegration, as radium, ionium, etc., has separated also, of which after a few thousands of years nothing would be recognisable but the helium to which it had given rise. F. S.

The Absorption of Radium Emanation by Cocoanut Charcoal. JOHN SATTERLEY (*Phil. Mag.*, 1910, [vi], **20**, 778—788).—The first point tested was whether the same fraction of radium emanation, whatever the amount may be, is absorbed by charcoal when the experimental conditions are the same. For solutions of strengths 3×10^{-9} and 6×10^{-9} gram of radium, but not for stronger solutions, proportionality between the emanation retained and the amount of radium present held good, justifying the method previously employed (Abstr., 1908, ii, 918). With a steady source of emanation the fraction absorbed decreases with the length of the experiment, as though the charcoal became saturated. The humidity of the air stream made no difference. A constant air stream was sent through two charcoal tubes in series. The ratio of the amount of emanation absorbed in the second to that in the first rose with the time of experiment. With tubes 8 sq. cm. in cross section containing 30 cm. length of coarsely powdered cocoanut charcoal, and an air stream 0·5 litre per minute continued twenty-one hours, 62 per cent. of the total emanation is absorbed. For air streams 0·11, 0·25, and 0·80 litre per minute, the fractions absorbed were respectively 0·86, 0·73, and 0·23. F. S.

The Relation between Uranium and Radium. V. FREDERICK SODDY (*Phil. Mag.*, 1910, [vi], **20**, 340—342).—The rate of growth of radium in the three uranium solutions, which previously had proceeded according to the square of the time (compare this vol., ii, 10), has since not been maintained, and it has been found that the constant of the electroscope employed has changed, the instrument now being about 10% more sensitive than at first. Previous estimates of the period of the parent of radium (ionium) are therefore in error, the data still only affording the means of calculating the minimum period of the long-lived intermediate substance, assuming there is but one, and not as proving the production of radium from the uranium. The minimum period from present results is 35,000 years, and the true period may be much greater. A method of obtaining an upper limit for the period from a study of the intensely active ionium preparations separated from thirty tons of pitchblende by the Austrian Government is given. F. S.

The Rays and Products of Uranium-*X*. II. FREDERICK SODDY (*Phil. Mag.*, 1910, [vi], **20**, 342—345).—The preparations of uranium-*X* previously described (this vol., ii, 10) have now been under observation for periods of a year to eighteen months, and in none has there been any increase of the initial α-radiation present, which is ascribed to an impurity present from the start in the uranium. This is in agreement with the revised estimate for the minimum period of ionium (compare preceding abstract), for if this is greater than 35,000 years the detection of the ionium produced from the uranium-*X* by means of its α-rays would not be possible with the arrangements employed. The proportion of β-rays in the radiation of uranium possessing an apparent value for $H\rho$ above 8640 is given as 1/750th. Tests to see whether actinium is produced from the uranium-*X* pre-

parations have so far given negative results. Actinium is present in all the preparations, but it is ascribed to initial impurities in the uranium.

F. S.

The Ratio between Uranium and Radium in Minerals FREDERICK SODDY and RUTH PIRRET (*Phil. Mag.*, 1910, [vi], 20, 345—349).—Determinations are given of the ratio of radium to uranium in autunite and thorianite (compare Mlle. Gleditsch, Abstr., 1909, ii, 714). The ratio for thorianite was found to be only 3% higher than for Joachimsthal pitchblende, while for autunite (of Portuguese origin) it was very low, being only 44·5% of that of pitchblende. The natural explanation is that autunite is of such recent formation that the uranium-radium series is not yet in equilibrium. The specific α-activities of the oxides of uranium separated from autunite, pitchblende, and thorianite were practically the same, which excludes the possible explanation that the variations in the uranium-radium ratio are due to two successive slow α-changes in uranium itself.

F. S.

Selective Photo-electric Effect of Potassium Mercury Alloys. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1910, 12, 697—710. Compare this vol., ii, 379—472).—The photo-electric sensitiveness of potassium amalgams of varying composition has been investigated. Amalgams containing 2·5 to 17·3 atoms % of potassium do not exhibit the selective effect at $\lambda = 436$ $\mu\mu$ which is characteristic of potassium. This selective action is, indeed, no longer found in the case of either liquid or solid alloys containing as little as 21 atoms % of mercury.

For alloys containing from 17 to 70 atoms % of potassium a selective effect has been found in the neighbourhood of $\lambda = 386$ $\mu\mu$, and for alloys which contain from 5 to 10 atoms % of potassium it is probable that there is a further characteristic photo-electric effect at about $\lambda = 313$ $\mu\mu$. The selective effect at λ 386 $\mu\mu$ is supposed to be due, at any rate in the case of the solid alloy, to the compound KHg.

H. M. D.

The Ionisation Produced by the Splashing of Mercury. J. J. LONSDALE (*Phil. Mag.*, 1910, [vi], 20, 464—474).—The ions produced by splashing have been usually examined for volatile liquids, and have been found to move with very small velocity. Hence mercury was tried to see if this was due to condensation of vapour on the ions. The results were found to be independent of electrification of the mercury and of its purity, but depended on the nature of the splash-plate. With iron the positive ions were in great excess. Cleaning the plate did not much affect the positive ionisation, but reduced the negative. Platinum gave smaller positive and negligible negative, mercury negligible positive but larger negative, ionisation. The minimum mobility of the ions with iron splash-plate was 0·013 (cm. per volt-cm.) for the positive and 0·004 for the negative. But in the former case the saturation curve showed a second maximum, due either to ions of

smaller mobility or to neutral doublets broken up by the action of the field. The latter explanation was favoured by further experiments, negative ions in some cases being initially absent, but produced in the gas by the application of a field. The negative ions appear to arise altogether from the breaking up of the doublets. By varying the height of fall of the mercury, it was found that no slow positive ions and no negative (therefore no doublets) are produced when the height is below 21·5 cm. The saturation curves, when heated aluminium phosphate or lime was used as the source of the ionisation, showed similar peculiarities for the positive ions. F. S.

Specific Change of the Ions Emitted by Hot Substances. II. OWEN W. RICHARDSON and E. R. HULBIRT (*Phil. Mag.*, 1910, [vi], **20**, 545—559. Compare Abstr., 1908, ii, 1009).—The ratio of the charge to the mass for the positive ions emitted by heated metals has been determined for platinum, palladium, gold, silver, copper, nickel, iron, osmium, tantalum, tungsten, brass, "nichrome," and steel. From this the mass of the ion in terms of the hydrogen atom as unity is deduced, on the assumption that unit charge is carried. A correction reducing the values to 0·62 of the experimental is made, because the value for the negative ion from platinum found by the same apparatus and method was wrong to this extent. The general result is to show that the mass of the positive ion from all substances is of the same order, the mean value being 23·3. Some of the substances proved difficult on account of irregularities in the ionisation, and because the initial value was different from the values after some heating. The suggestion is made that the positive ionisation is due to sodium as a common impurity in all the metals. F. S.

Positive Electrification due to Heating Aluminium Phosphate. A. E. GARRETT (*Phil. Mag.*, 1910, [iv], **20**, 573—591).—When aluminium phosphate is heated at about 1200°, large numbers of positive ions are emitted, and this phenomenon has been investigated by measuring the conductivity imparted to the surrounding gaseous atmosphere. The emission effect decays with time, and the activity of the substance at any moment can be represented by an expression of the form: $A(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + B(1 - e^{-\lambda_3 t})$. During the first portion of the period of decay, the nature of the surrounding gas and the traces of water present in the active substance have a marked influence on the form of the decay curve. This is no longer evident when the steady state has been reached.

For a given temperature, the current due to the positive ions has a maximum value for a particular pressure; this pressure diminishes as the temperature is raised. At constant pressure the relationship between the current and the absolute temperature can be expressed satisfactorily by means of Richardson's formula.

Measurements of the value of e/m show that the smallest positive ions, which are emitted at the lowest pressures, are comparable in size with the hydrogen atom. In consequence of the high velocity of the ions at low pressure, even in the absence of an external field, a tube

containing strongly heated aluminium phosphate can be used as a rectifier for alternating currents.

Observations are also recorded which seem to show that neutral doublets as well as ions are emitted by the heated substance.

H. M. D.

The Electrical Conductivity of Liquid Alloys. KARL BORNEMANN and PAUL MÜLLER (*Metallurgie*, 1910, 7, 396—402).—Very few data exist as to the electrical conductivity of liquid alloys. The experiments described have been made in glass or quartz tubes, heated in an oil-bath or an electric furnace, according to the temperature required. Iron, platinum, or carbon electrodes are used, auxiliary electrodes being introduced in quartz tubes at different points for the measurement of the fall of potential.

The liquid alloys of sodium and potassium give a conductivity-concentration curve which exactly resembles that typical of a continuous series of solid solutions, such as gold and silver. The conductivity of each liquid metal is lowered by the addition of the other, and the curve has a well-marked minimum. There is no indication of the compound Na_2K, the existence of which is shown on the freezing-point curve as a change of direction, and it therefore appears that this compound is much dissociated in the molten alloys.

On the other hand, liquid alloys of lead and tin exhibit a conductivity which varies with the concentration in an almost perfectly linear manner. The curves of temperature-coefficients of the conductivity follow a similar course to the conductivity curves.

Sodium amalgams exhibit a depression of conductivity at both ends of the series, rising to an intermediate maximum at a point corresponding with the compound $NaHg_2$, which probably exists in the liquid in a largely undissociated condition, as evidenced by the very high freezing point of the compound in comparison with those of its components. A similar, but less marked, maximum is caused in the amalgams of potassium by the compound KHg_2. A new criterion for the existence of compounds in solution is thus obtained.

Observations on dilute amalgams show that the conductivity of mercury is lowered by the addition of either of the alkali metals, but the older observations, that the conductivity is raised by the addition of other metals, are confirmed. The abnormally low temperature-coefficient of mercury (0·001) was attributed by Liebenow to the presence in the liquid of two or more different kinds of molecules, giving it the properties of an alloy. In accordance with this view, the addition of the alkali metals, which form compounds with mercury, and thus increase the number of complex molecules, lowers its conductivity, whilst the indifferent metals, which dissolve in the monatomic form, raise it. It is shown that lead, which has an even lower temperature-coefficient than mercury, has its conductivity raised by the addition of metals which do not combine with it, such as zinc, cadmium, antimony, and bismuth, although the conductivity of bismuth is less than that of lead. Potassium and sodium have a normal temperature-coefficient (0·004), and their conductivity is

lowered by the addition of other metals, whether they form stable compounds or not.

Heterogeneous mixtures of liquid metals, such as lead and zinc, have a conductivity strictly proportional to the concentration, whether the liquids are emulsified or in distinct layers. The temperature at which the separation of a homogeneous liquid alloy into two layers takes place may be determined more accurately by the conductivity than by the thermal method, being indicated by an abrupt change of direction in the conductivity-temperature curve. C. H. D.

The Electrical Conductivity and Hardness of Alloys of Silver and Copper. NIKOLAI S. KURNAKOFF, NIKOLAI A. PUSHIN, and N. SENKOWSKY (*Zeitsch. anorg. Chem.*, 1910, **68**, 123—140; *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 733—751).—The electrical conductivity and hardness of the alloys of silver and copper have been re-determined with special precautions. The conductivity falls from that of pure copper until 4 atomic % Ag is reached, after which it remains nearly constant until 91 atomic % Ag is reached, and then rises rapidly to that of pure silver. The curve for hard-drawn wires closely resembles that for the annealed metals, but the conductivity is throughout lower. The curves representing the temperature-coefficient of the conductivity have exactly the same form.

The determinations of hardness are best made by means of Brinell's ball test on specimens annealed at 650—700°. The curve obtained is the converse of the conductivity curve, and indicates the same limits of concentration of the solid solutions, namely, 0—4 and 91—100 atomic % Ag. The alloys thus represent the simplest type of a series composed of two solid solutions separated by a gap.

C. H. D.

Conduction of Electricity Through Solid Silver Chloride. II. MAX LE BLANC and FRITZ KERSCHBAUM (*Zeitsch. Elektrochem.*, 1910, **16**, 680—681).—The conductivity of solid silver chloride produced by prolonged treatment with continuous current (this vol., ii, 382) is shown to be due to excessively thin threads of metallic silver. T. E.

Potential of Iron Calculated from Equilibrium Measurements. ARTHUR B. LAMB (*J. Amer. Chem. Soc.*, 1910, **32**, 1214—1220).—Richards and Behr (Abstr., 1907, ii, 222) have found that the true potential of iron is 0·18 volt for the porous form, and 0·15 volt for the massive form, the calomel electrode being taken as $-0·56$ volt, whilst other authors have obtained values about 0·1 volt lower.

A calculation from existing data has now been made, which shows that the potential of iron against a molecular normal solution of ferrous ions is 0·192 volt, the calomel electrode being taken as $-0·564$ volt. E. G.

Evolution of Gas and Capacity of the Lead Accumulator. FRANZ STREINTZ (*Zeitsch. Elektrochem.*, 1910, **16**, 747—754).—The quantities of oxygen and hydrogen evolved during the charge of a

small accumulator are compared with those given off from platinum electrodes through which the same current passes. The differences give the capacities of the plates, and these are compared with the capacity of the accumulator when discharged. About 94% of the charge is obtained from the lead plate and about 87% from the lead peroxide plate. It is also shown that the fully charged plates continue to absorb a little hydrogen or oxygen if the charging current is continued. In the case of the lead plate, this is due to occlusion of hydrogen; in that of the lead peroxide plate, it is due to slow oxidation of the lead framework supporting the peroxide. T. E.

Chemical Action of the Silent Electrical Discharge. A. MOSER and N. ISGARISCHEFF (*Zeitsch. Elektrochem.*, 1910, **16**, 613—620).—Various gases are submitted to the action of the silent discharge in ordinary ozone-tubes. The current and the voltage are measured, and also the temperature and pressure of the gas in the tube.

When pure carbon dioxide or a mixture of carbon monoxide and oxygen (2 vols. : 1 vol.) is used, an equilibrium is attained which depends on the voltage used, the temperature, and the distance apart of the electrodes. Only traces of ozone are formed, and the same equilibrium is attained in presence of chlorine, but much more slowly. If excess of carbon monoxide or oxygen is used, either the brown solid formed from carbon monoxide alone or ozone is produced. With about 6000 volts at 20° and the electrodes 1·7 mm. apart, about 14% of the carbon dioxide is dissociated when equilibrium is attained. This increases with increased voltage, and diminishes at higher temperatures and with increased distance apart of the electrodes. The quantity dissociated is from thirty to one hundred times more than would be calculated from Faraday's law, but the free energy of the carbon monoxide and oxygen produced is only from 1·2 to 6·3% of the electrical energy expended in producing the decomposition.

The decomposition of hydrogen chloride is very small (about 1% with 14,000 volts).

Sulphur dioxide and oxygen combine quantitatively to form the trioxide. The yield of sulphur trioxide per kilowatt hour varies from 3·5 to 14·3 grams.

A mixture of hydrogen chloride and oxygen is converted largely (95%) into chlorine and water, 10 to 13 grams of chlorine per kilowatt hour being formed. T. E.

The Oxygen Electrode. Electromotive Behaviour of the Oxides of Platinum. G. GRUBE (*Zeitsch. Elektrochem.*, 1910, **16**, 621—632).—The measurements of the potentials of platinum oxide electrodes made by Lorenz (Abstr., 1909, ii, 463, 640, 857) may be too low, owing to the lack of conductivity of the oxides and to the fact that in one set of measurements the electrodes were yielding a small current. The author has made measurements on electrodes containing several grams of the oxide mixed with graphite and compressed in a perforated platinum foil case. The results, referred to the hydrogen electrode for 2*N*-sulphuric acid at 18°, are: $PtO_2,4H_2O$, 1·06 volts; $PtO_2,2H_2O$, 1·04 volts; PtO_3, about 1·5 volts; PtO,

indefinite, about 0·9 volt. An electrode containing the trioxide evolves oxygen continuously, and its potential falls slowly. An electrode of the dioxide when polarised anodically behaves in the same way as one made of the trioxide. A monoxide electrode when anodically polarised possesses, at first, a higher potential than the dioxide, which falls off steadily.

The potential of a platinised platinum electrode after anodic polarisation was followed for two hundred and sixty-two days. It fell quite steadily from 1·5 volts to 1·05, at which point it remained for eight days, then falling to 1·02 volts, where it remained without further change.

It appears, therefore, that potentials from 1·5 volts downwards are due to solid solutions of PtO_3 in PtO_2, or of PtO_2 in PtO.

Since platinum electrodes can be polarised up to potentials of 2 volts, it appears probable that an unknown tetroxide of platinum may exist. T. E.

Anodic Behaviour of Molybdenum, Manganese, Chromium, and Tantalum. HANS KUESSNER (*Zeitsch. Elektrochem.*, 1910, **16**, 754—772).—A molybdenum anode dissolves quantitatively, with the valency 6, in *N*-potassium hydroxide. The metal used contained a little iron and traces of carbon and oxide, but two different pieces of it behaved differently. One of them became passive when the current density exceeded about 0·05 ampere per sq. cm., whereas the other showed no signs of passivity with very much larger current densities.

With a manganese anode in neutral solutions (of potassium chloride or sulphate). the metal dissolves, and both hydrogen and oxygen are evolved, the whole of the metal finally present in the solution being bivalent. Manganese itself dissolves with evolution of hydrogen, but the rate is too slow to account for the quantities of hydrogen observed; it is, therefore, thought probable that univalent manganese ions are formed which react with the hydrogen ions in the solution thus: $2Mn^{\cdot} + 2H^{\cdot} = 2Mn^{\cdot\cdot} + H_2$. From 8—10% of the manganese dissolves in this way. The oxygen is evolved when the potential of the manganese anode is more than 0·3 volt more negative than the normal hydrogen electrode, whilst hydroxyl ions could only be discharged directly if it were 1·62 volts more positive; the oxygen is, therefore, a secondary product. The potential measurements show further that the dissolution of manganese accompanied by evolution of oxygen at the anode and of hydrogen at the cathode is a process which takes place of its own accord; hence the gain of free energy due to the conversion of metallic manganese into ions cannot be less than the loss due to the decomposition of water. Following this out quantitatively, it appears that the manganese must dissolve primarily in the form of tervalent ions, which then react with hydroxyl ions, thus:

$$2Mn^{\cdot\cdot\cdot} + 2OH' = 2Mn^{\cdot\cdot} + H_2O + \tfrac{1}{2}O_2.$$

Increasing the alkalinity of the electrolyte leads to the formation of manganese ions of higher valency in increasing quantity.

A chromium anode in solutions of potassium chloride dissolves with different valencies between 2 and 6. At low temperatures and small

current densities the valency approaches 6; at higher temperatures it falls, but the author could not find any set of conditions in which only one kind of ion is formed. This was equally the case in alcoholic solutions of zinc chloride.

In 16*N*-solutions of potassium hydroxide a tantalum anode is converted into the pentoxide, the electro-chemical valency being 5. The pentoxide forms a layer on the anode which permits a small current to pass. Increasing the applied voltage does not increase this current beyond 0·02 to 0·03 ampere per sq. cm. T. E.

Migration of Ions in the Water Voltameter. FRANZ STREINTZ (*Zeitsch. Elektrochem.*, 1910, **16**, 744—747).—In Hofmann's voltameter, in the form commonly used for demonstrating the electrolytic decomposition of water, the sulphuric acid in the cathode tube rises, whilst that in the anode tube falls. The effect is measurable after one hour's electrolysis with 1 ampere or more. The author has compared the rise and fall (due to changes in the density of the acid) in a special apparatus with narrow tubes with those calculated from Hittorf's measurements of the migration of sulphuric acid, and has found a fairly close agreement. The changes of level are, however, larger than those calculated, instead of being smaller, owing to partial equalisation of the densities by diffusion. T. E.

Electrolysis of the Iodides of the Alkaline Earths Dissolved in Pyridine. GEORG VON HEVESY (*Zeitsch. Elektrochem.*, 1910, **16**, 672—673).—A saturated solution of barium iodide in pyridine contains 20·358 grams per litre at 25°. The conductivity per equivalent at 25° is: $v=9{\cdot}606$, $\Delta=8{\cdot}855$; $v=18{\cdot}01$, $\Delta=10{\cdot}723$; $v=38{\cdot}59$, $\Delta=13{\cdot}045$; $v=81{\cdot}06$, $\Delta=15{\cdot}961$.

When these solutions were electrolysed with platinum electrodes separated by a porous partition, a firmly adherent non-conducting deposit was very soon formed on the cathode. This consisted of barium hydroxide and carbonate, and was due to traces of moisture in the solutions. The pyridine was then dried completely by prolonged electrolysis with 110 volts, but the barium produced by the electrolysis of the dry solutions reacted with the pyridine itself, giving a reddish-brown slime; this was the case even at $-40°$.

A barium amalgam containing up to 30% of barium may be prepared by electrolysing the dry pyridine solutions with a mercury cathode, the current efficiency being about 80%. T. E.

Sparking at the Electrodes in the Electrolysis of Molten Salts. ANTON KAILAN (*Zeitsch. anorg. Chem.*, 1910, **68**, 141—159).—When molten chlorides are electrolysed with a carbon anode and an iron cathode, the operation is sometimes interrupted by the separation of the mass from the anode, the cessation of the evolution of chlorine, and a rapid fall of the current strength.

It is shown, by measurements of the fall of potential when chlorides are electrolysed, that the effect is not due to the formation of a subchloride, or to the separation of a layer of silica derived from the crucible. The effect is completely inhibited by increase of

temperature, a critical temperature being observed at 500° in a mixture of equal weights of potassium and lithium chlorides, and at about 590° in pure lithium chloride. The addition of lithium bromide hinders the effect. The effect of temperature appears to be connected with the change of viscosity, a conclusion which is confirmed by experiments with dilute sulphuric acid to which glycerol has been added. The effect occurs with a platinum anode as well as with carbon. When the effect is present, the apparent resistance of the cell falls with increasing potential difference. Experiments with an oscillograph show that the variations in the current are very small, provided that the anode dips sufficiently far into the electrolyte. There are about 2000 oscillations in a second. A purely mechanical explanation of the phenomenon is suggested. C. H. D.

Properties of Salt Solutions in Relation to the Ionic Theory. I. Mol-numbers Derived from the Freezing-point Lowering. ARTHUR A. NOYES and K. G. FALK (*J. Amer. Chem. Soc.*, 1910, **32**, 1011—1030).—This paper is devoted to a consideration of the lowering of freezing point caused by acids, bases, and salts, and includes a large number of numerical data collated from the best published observations. The symbol i has been employed to represent the factor by which the number of formula weights, N, associated with 1000 grams of water must be multiplied if the osmotic pressure is to be correctly calculated by the laws of a perfect solution. This has been calculated for several substances in dilute aqueous solution from the simplified equation: $iN = \Delta t/1{\cdot}858.(1 + 0{\cdot}0055\Delta t)$, deduced from Washburn's expression (*Tech. Quart.*, 1908, **21**, 273); Δt is the lowering of freezing point.

The principal table contains the values of the ratio $\Delta t/N$ (called the formal freezing-point lowering) for forty-two substances, also the weighted mean of several determinations, the best value for the ratio, and finally the mol-number, i, in each case for concentrations between 0·005 and 0·5 equivalent per 1000 grams of water.

The author utilises the results in the discussion of the relation of the mol-number to the type of salt and its variation with concentration. W. O. W.

Elevation of Boiling Point under Reduced Pressure. KARL DRUCKER (*Zeitsch. physikal. Chem.*, 1910, **74**, 612—618).—An apparatus for measuring the elevation of the boiling point under reduced pressure, similar to that used by Rose-Innes (Trans., 1902, **81**, 682), is described and figured. As in Beckmann's most recent form of apparatus, electrical heating is used.

The apparatus has been tested with benzene, chloroform, and alcohol as solvents, and camphor as solute with satisfactory results. The observed values of the elevation and those calculated by the van't Hoff formula are in excellent agreement for benzene and for alcohol, but not for chloroform. The experimental value for the latter at 61° is 39·1, in agreement with recent measurements of Beckmann and of Turner (Trans., 1910, **97**, 1184), whilst the calculated value at the same temperature is 38·3. G. S.

Vaporisation in Vacuum. JAROSLAV HLADÍK (*Biochem. Zeitsch.*, 1910, **28**, 29—33).—An apparatus is described for the rapid evaporation of solutions under reduced pressure. The vapour is condensed on the inner surface of a cooled bell-shaped vessel, which forms the upper part of the vaporising chamber. The condensed liquid collects in a circular trough which communicates with a collecting bottle outside, through which communication is made with a pump for exhausting the apparatus. H. M. D.

Binary Solution Equilibria of the Three Isomeric Nitroanilines. ROBERT KREMANN (with J. GEBA and F. NOSS) (*Monatsh.*, 1910, **31**, 855—859).—The melting-point curve for mixtures of *o*- and *m*-nitroanilines falls from the melting point of each component to a eutectic point at 47°, the eutectic composition being 66% of *o*-nitroaniline. *m*- and *p*-Nitroanilines give a similar curve, the eutectic temperature being 86°, and eutectic composition 66% of *m*-nitroaniline. Similar results are obtained with mixtures of *o*- and *p*-nitroanilines, the eutectic temperature and composition being 52° and 78% *o*-nitroaniline respectively.

The irregular curves obtained by Tingle and Rolker for these substances (Abstr., 1908, i, 408, 974) are due to the fact that small quantities were used, and the melting points determined by the ordinary method employed in organic chemical practice. T. S. P.

A Simple Distillation Apparatus. F. VOLLRATH (*Chem. Zeit.*, 1910, **34**, 1068).—A simple substitute for a condenser is described, consisting of a bottle with double-bored cork, through one hole of which the tube from the distilling flask enters, whilst the other is fitted with a funnel, in which a flask filled with cold water rests.

C. H. D.

Adiabatic Determination of Heats of Solution of Metals in Acids. II. Heat of Dilution of the Acid Solutions. THEODORE W. RICHARDS, ALLEN W. ROWE, and LAURIE L. BURGESS (*J. Amer. Chem. Soc.*, 1910, **32**, 1176—1186).—In an earlier paper (this vol., ii, 391) an account was given of a series of determinations of the heat of solution of zinc, aluminium, magnesium, cadmium, and iron in an excess of hydrochloric acid at 20°. In the course of this work, it was found that the heats of dilution, both of the acids and of the residual solutions after the completion of the reactions, affect the results to a considerable extent. In order to reduce to the same standard, it was therefore necessary to carry out experiments on the heats of dilution, and an account of this work is now presented.

The heats of dilution at 25° of the acids $HCl,20H_2O$ and $HCl,8·808H_2O$ to $HCl,200H_2O$ were determined, and found to be 0·556 and 1·330 Cal. (or 2·32 and 5·56 kilojoules) respectively. The heats of dilution of the products obtained by dissolving zinc, aluminium, cadmium, and iron in excess of concentrated acid were determined. The substitution of salt for acid was found to affect seriously the heat of dilution, especially in the cases of zinc and cadmium. From these data, the heats of solution of a gram-atom of the five metals in exactly

the theoretical quantity of $HCl,200H_2O$ have been calculated, and are given in 18° Cals. and also in kilojoules: zinc, 36·6 Cal. or 153·1 kilojoules; aluminium, 127·0 Cal. or 531·0 kilojoules; magnesium, 110·2 Cal. or 460·6 kilojoules; cadmium, 17·2 Cal. or 71·9 kilojoules; and iron, 20·8 Cal. or 87·0 kilojoules. E. G.

Effect of the Glass Surface in Vapour Density Determinations. KARL DRUCKER and G. ULLMAN (*Zeitsch. physikal. Chem.*, 1910, **74**, 567—611).—The densities of the vapours of a number of organic compounds at varying temperatures and pressures have been investigated by a modification of the Hofmann method under such conditions that the influence of the glass surface could be determined. The glass surface was varied by using different quantities of glass wool in the interior of the density bulb. The method of measurement adopted is described in detail. The corresponding measurements of Ramsay and Steele (Abstr., 1903, ii, 635) are affected by a considerable error, owing to inaccurate determination of the temperature of the mercury column in the measuring tube.

From the results, the percentage values of pv as compared with that for an ideal gas are calculated and plotted as ordinates against the corresponding pressures as abscissæ. The vapours of benzene, ethyl ether, chloroform, and ethyl alcohol are adsorbed to a small extent on the glass surface, but the adsorption can be neglected for ordinary measurements. Acetic acid, on the other hand, is condensed very considerably; this adsorption is not satisfactorily represented by the ordinary adsorption formula with coefficient less than unity. From the results, the complex constant $k = [\text{bimolecular acid}]/[\text{unimolecular acid}]^2$ has been obtained. At 110°, 95·5°, and 80·2° the values of k are 0·11, 0·25, and $0·60 \times 10^3$ respectively. The alteration with temperature is much smaller than that observed by Ramsay and Steele.

Ramsay and Young state that the saturated vapour of acetic acid shows a minimum in the density with change of temperature, but the authors point out that the extrapolation of Ramsay and Young leads to inaccurate values, owing to the influence of adsorption, and that there is no real abnormality of the nature indicated.

The thickness of the layer of acetic acid on the surface of the measuring tube is 0·16—0·60μ, that of chloroform 0·10—0·20μ, and that of alcohol only 0·004—0·011μ. G. S.

van Laar's Theory of the Contraction in Water-Alcohol Solutions. A. G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 442—452. Compare van Laar, Abstr., 1900, ii, 189).—A theoretical discussion of van Laar's theory of the association of liquid molecules, in which the authors conclude that van Laar has given no proof of the fundamental principles underlying his theory. Using van Laar's formula for mixtures of water with propyl and *iso*propyl alcohols, the contraction of volume of the water, which, according to van Laar, should equal 8·44 at 15 56°, is only 4·67 for the former and 4·79 for the latter; on the other hand, the contraction with ethyl alcohol at 20° is 8·31. Z. K.

Molecular Volumes of Solids. H. H. STEPHENSON (*Chem. News*, 1910, **102**, 178—180, 187—189).—Regularity may be traced in the molecular volumes of solids without departing from the atomic volumes of the free elements. Molecular condensation is defined, and shown to be equal for anhydrous salts in each group or sub-group of the Periodic Table for each class of compound, but to vary with the groups and with the acid radicle. The density and molecular volume of any solid compound may, therefore, be calculated if the group condensation is known. The atomic volumes of elements may also be obtained from the density of any of their compounds; for instance, ytterbium has an unknown atomic volume, but its oxide, Yb_2O_3, has a molecular volume of 43, and the condensation of the sesquioxides of its group is 48, which gives Yb = 19·8, showing a density of 8·7. Hydrated salts, double salts, acid and basic salts, are generally additive in molecular volume, the value for each molecule of water averaging 14. Formulæ are given connecting the densities of hydrated and anhydrous salts. It is also shown that the apparent equality of volume of some series of similar and isomorphous salts is due to the fact that they have undergone equal condensation from approximately equal theoretical volumes.

W. P. S.

The Equation of Continuity of the Liquid and Gaseous States of Matter. RICHARD D. KLEEMAN (*Phil. Mag.*, 1910, [vi], **20**, 665—689).—A mathematical paper in which the expression deduced previously for the attraction between two molecules is made the starting point for the deduction of equations relating to the continuity of the liquid and gaseous states of aggregation. Certain of these relationships are examined by reference to experimental data for various organic compounds. H. M. D.

Surface Energy and Surface Tension. JAMES E. MILLS and DUNCAN MACRAE (*J. Amer. Chem. Soc.*, 1910, **32**, 1162—1176).—Whittaker (Abstr., 1908, ii, 817) has stated that the surface energy of a liquid in contact with its own vapour at any temperature is proportional to the product of the internal latent heat and the absolute temperature. This relation has now been investigated, and found to be only approximately true. It is shown that the relation suggests a division of the so-called surface energy of a liquid into two parts, one due to the liquid surface and the other to the surface of the vapour over the liquid, and this point will be further investigated.

E. G.

Measurement of Surface Tension by the Method of Maximum Pressure of Small Bubbles. R. MAGINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 184—189).—By the adoption of certain improvements in the experimental arrangements, the author has succeeded in obtaining by this method (compare Cantor, *Ann. Phys. Chem.*, 1892, [ii], **47**, 399, 422; Feustel, *Ann. Physik*, 1905, [iv], **16**, 61) measurements of the surface tension of benzene, nitrobenzene,

liquid air, and water, with a degree of exactness comparable with that obtained by Rayleigh's wave method (compare Abstr., 1907, ii, 334).

R. V. S.

Surface Tension of Aqueous Solutions and Laplace's Constant. WILLIAM C. McC. LEWIS (*Zeitsch. physikal. Chem.*, 1910, 74, 619—640).—It has already been shown that whilst inorganic salts increase the surface-tension liquid/vapour, they diminish the surface-tension liquid/liquid. In this connexion the surface-tension liquid/vapour has been measured by the dropping method for rosaniline hydrochloride, Congo-red, methyl-orange, methyl-violet, sodium glycocholate, carbamide, malonic acid, and copper sulphate at 14°, 43°, 61°, and 78°. The action of the dissolved substances diminishes gradually as the temperature rises, but in no case has an inversion been observed.

The different effect of inorganic salts in the two cases is discussed and accounted for on the basis of Laplace's theory of internal pressure. Employing instead of the surface-tension, σ, Laplace's capillary factor H_0, where $\sigma = H_0\rho^2/2$, ρ being the density, it is shown that H_0 for water is diminished by the addition of all dissolved substances, both at the surface liquid/liquid and at the surface liquid/vapour. With reference to the specific internal pressure K_0 (where $K = K_0\rho^2$), it is shown that with the exception of those liquids which are completely miscible with water, the addition of any dissolved substance to water diminishes the value of K_0, whereas, according to Tammann, in the same circumstances, K always increases.

Considering only the surface liquid-vapour, it is shown that the changes of the internal pressure, K, and the surface tension, σ, are always in the same direction. This rule does not apply when the solute is volatile or for certain colloidal solutions.

The considerable diminution of the surface tension produced by certain solutes can be accounted for on the basis of Laplace's theory.

G. S.

The Physico-chemical Theory of Soap Emulsions. Emulsification of Hydrocarbon Oils by Aqueous Solutions of Salts of the Fatty Acids. FREDERICK G. DONNAN and H. E. POTTS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 208—214).—The influence of the sodium salts of eleven normal fatty acids on the surface tension at the contact surface between water and a nearly acid-free hydrocarbon oil has been investigated. The fatty acids used formed a continuous series from acetic to decoic, and, in addition, lauric and myristic acids were examined. All these salts diminish the surface tension, and the extent of the diminution increases in general with increasing molecular weight of the acid. The action begins to be considerable in the case of sodium octoate, and from this point onwards the influence increases more and more rapidly as the molecular weight increases. In harmony with these observations, it is found that the sodium salts of lauric and myristic acids are the only members of the series which give rise to emulsification effects. In these two cases the emulsification capacity increases rapidly with the concentration of the dissolved salt, and then decreases rapidly at higher coucentrations. The existence of this

maximum effect is attributed to the salting-out action of the sodium ions. It is supposed that the changes in surface tension, which are obviously connected with the emulsifying power of certain solutions, are accompanied by changes in the potential differences at the contact surface. H. M. D.

Autosorption (Auto-adsorption). WILLIAM C. McC. LEWIS (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 197—205).—The views expressed in this paper relating to the nature of the liquid vapour contact surface have been for the most part published previously (compare this vol., ii, 829). The term autosorption is introduced in reference to the greater density of the surface layer of a liquid as compared with its bulk density. Whereas autosorption has been found for a number of liquid organic compounds which have been examined, there appears to be little difference in the surface and bulk densities in the case of the elements mercury, bromine, and iodine. For these substances the autosorption is therefore of very small magnitude, and this appears to be the case for zinc and cadmium.

The surface and bulk densities of water are employed to calculate the difference between the quantity of water actually present in the surface layer of water and that which would be present if capillary forces were eliminated. The value thus obtained is of the order 10^{-6}—10^{-7} gram per sq. cm. H. M. D.

Changes in Tanning [Processes]. REGINALD O. HERZOG and GEORG ROSENBERG (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 222—227). —In continuation of previous experiments (Abstr., 1908, ii, 262) on the adsorption of substances from aqueous solution by lightly chromed hide powder, the authors have made similar measurements with non-chromed powder. Aqueous solutions of sodium picrate, silver nitrate, crystal-violet, patent-blue, new-magenta, and phenol were examined. The removal of sodium picrate from aqueous solution takes place in accordance with the simple law of distribution, the value of the exponent in the adsorption formula being equal to unity. With chromed hide powder the proportion of adsorbed substance increases somewhat with the concentration of the solution. In the case of silver nitrate, the data agree with the formula $K = B^m/C$, in which C is the quantity of the adsorbed substance, and B is the concentration of the residual solution, if m is made equal to 0·5. The adsorption of the three colouring matters is also in accord with the exponential equation, but the data for phenol show considerable divergence, and this is considered to indicate that the removal of phenol by the hide powder is not due to a simple adsorption process. An empirical formula is given by means of which the data for phenol can be satisfactorily reproduced.

In general, there is no essential difference in the behaviour of chromed and non-chromed hide powder in regard to their adsorptive properties. H. M. D.

The Capillary Rise of Acids. ZDENKO H. SKRAUP, E. KRAUSE, and A. VON BIEHLER (*Monatsh.*, 1910, **31**, 753—776).—In the case of all organic acids, the regularities which have been previously observed

are confirmed (compare Abstr., 1909, ii, 868; this vol., ii, 191). The stronger the acid is, the more it is absorbed by the filter paper, and the less is the capillary rise; the weaker it is, the less is the absorption. The large capillary rise with acetic acid is much diminished when it is transformed into trichloroacetic acid; the same result is true for the pairs of acids: succinic and dibromosuccinic; benzoic and nitrobenzoic.

Phosphoric acid has a very small capillary rise, and the suggestion has been made that this is due to its polybasicity. In order to test the validity of this suggestion, measurements have been made with benzene-mono-, di- and tri-sulphonic acids, with different carboxy-acids of benzene, including mellitic acid, and with oxalic, malonic, succinic, glutaric, and tricarballylic acids. It is found that a decrease in the capillary rise does not take place with increase in the basicity of the benzenesulphonic acids; it does take place with the carboxy-acids of benzene, but the decrease stops when the value of the capillary rise becomes the same as that for strong acids. In the case of tricarballylic acid, the capillary rise is greater than that for malonic, succinic, or glutaric acids.

Arsenic acid is similar to phosphoric acid, in that it has an abnormally low capillary rise. Pyrophosphoric acid, in contradistinction to orthophosphoric acid, shows an abnormally high rise, whereas metaphosphoric and phosphorous acids give much lower rises, the rise with the latter acid approximating to that for relatively strong acids. Hydrofluoric acid gives practically the same result as hydrochloric acid, although it is much less dissociated.

Using a modification of Holmgren's circle method, the absorptions of sulphurous and hydrocyanic acids and solution of hydrogen sulphide have been investigated. Hydrocyanic acid has a higher capillary rise than hydrochloric acid, whereas with the other two acids the rises are practically the same as for hydrochloric acid.

The present investigation shows that there are undoubted regularities in the case of organic acids, but with inorganic acids the number of irregularities has been increased. T. S. P.

Osmotic Equilibrium between Two Fluid Phases. L. GAY (*Compt. rend.*, 1910, **151**, 612—616).—A purely mathematical treatment of the subject. W. O. W.

Relation of Osmotic Pressure to the Intrinsic Pressure of Liquids. M. M. GARVER (*J. Physical Chem.*, 1910, **14**, 651—664. Compare this vol., ii, 398).—The intrinsic or internal pressure of a gas in which the molecules exercise no attraction for one another is numerically equal to the extrinsic pressure exercised by the gas on the containing vessel. The intrinsic pressure of a liquid is equal to the extrinsic pressure plus the effect of molecular attractions, and has a different value in the surface film where molecular attractions are not wholly balanced.

The author assumes that the average molecular energy of translation is the same in the gaseous and liquid phases if the molecular

weight (m) is the same, since the mean square of the molecular velocity (v) in either phase represents the absolute temperature.

If p_1 and P_1 are the intrinsic pressures of gas and liquid respectively, $P_1 = \frac{2}{3}(n_2mv^2)/2 = \frac{2}{3}(n_1mv^2)/2 \times n_2/n_1 = p_1 \times n_2/n_1$, where n_2 and n_1 are the numbers of molecules per unit volume in liquid and vapour phase respectively. The intrinsic pressure of a liquid is very simply obtained by multiplying the vapour pressure by the ratio of densities of liquid to vapour. Further, it is deduced that $PV = pv = RT$, that is, the gas laws hold for liquids if P is interpreted as intrinsic pressure. If P_1 and P_2 be the intrinsic pressures of a solvent and solution respectively, $P_1 - P_2 = \rho RT/m \log_e p_1/p_2$ = the osmotic pressure, where p_1 and p_2 are the vapour pressures ot solvent and solution respectively. Osmotic pressure is thus defined as the reduction in intrinsic pressure or normal activity of the solvent due to the introduction of the solute. This reduction is brought about by the reduction of the number of molecules of solvent from N to $(N-n)$, n being the solute molecules. The volume concerned in osmotic calculations is the volume of the solvent multiplied by N/n, whilst the pressure is diminished in the ratio n/N.

The intrinsic pressure of water at 0° is 1235 atm. A weight-normal solution contains 1 molecule of solute to 55·6 of solvent, and its osmotic pressure is therefore 1235/55 6 = 22·2 atm.

If the membrane is not wetted by the liquid, a surface film exists, which with its unbalanced molecular attractions prevents free circulation of the solvent so that no osmosis occurs. The principal part in osmotic phenomena is played by the solvent, and some form of association hypothesis is necessary. R. J. C.

Methods of Diffusion Experiments. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 219—222).—The nature of the precipitation membranes which are formed when gelatin solutions of silver nitrate and the halogen salts of the alkali metals are juxtaposed is shown to depend on the circumstances in which the diffusion processes take place. H. M. D.

Inconstancy of the Solubility Product. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1910, **32**, 1186—1193).—Cameron (Abstr., 1902, ii, 75) has found that the solubility of gypsum is increased by addition of sodium chloride up to a certain concentration, and that beyond this point the solubility diminishes. Hill and Simmons (Abstr., 1909, ii, 647) have observed a similar behaviour when silver sulphate is treated with nitric acid solutions. It is shown that this decrease in total solubility can only be accounted for by assuming that the concentrations of the ions of the solute have diminished, and that the value of the solubility product has accordingly been reduced. The work now described was carried out with the object of gaining further evidence on this point.

The solubility of thallous chloride in acetic acid of concentrations between zero and $16N$, and that of tetramethylammonium iodide in potassium hydroxide of concentrations between zero and $8·3N$, has been determined at 25°. Measurements of the conductivity of a

saturated solution of tetramethylammonium iodide and of solutions varying from $N/8$ to $N/1024$ have also been made for use in the calculations. The results show that the solubility of thallous chloride and tetramethylammonium iodide is so diminished in presence of the other electrolytes as to prove conclusively that the solubility product is not a constant, but that it decreases with increase in the total concentration of electrolytes present. E. G.

Ionisation Relations of Sulphuric Acid. ARTHUR A. NOYES and M. A. STEWART (*J. Amer. Chem. Soc.*, 1910, **32**, 1133—1162).—Sulphuric acid is usually assumed to undergo ionisation in aqueous solution according to the equations: $H_2SO_4 = H^{\cdot} + HSO_4'$ and $HSO_4' = H^{\cdot} + SO_4''$, but the only investigation yielding valuable evidence as to the proportion of the HSO_4^- ion present is that of Noyes and Eastman *Carnegie Inst. Publications*, 1907, **63**, 239). The present work was therefore undertaken with the view of obtaining more definite information with regard to the ionisation of this acid.

The hydrogen-ion concentration, C_H, can be calculated from the value of the mol. number, i, as determined from the depression of the f. p., by means of the relation $C_H/C = i - 1$. The values of C_H/C at 0° have been thus derived from the recorded f. p. data.

It is shown that by combining conductivity and transference data, there can be derived maximum and minimum values of the hydrogen-ion concentration in sulphuric acid corresponding with the two limiting cases in which the only negative ion present is SO_4^- or HSO_4^-, and in this way limiting values of C_H/C at 25° and 0° have been calculated. Incidentally it has been found from a study of existing conductivity data at 0° that the best values for the equivalent conductivity at 0° of certain ions are $\Lambda_K = 40{\cdot}3$, $\Lambda_{Cl} = 41{\cdot}1$, $\Lambda_{SO} = 42{\cdot}8$, and $\Lambda_H = 224$.

The value of Λ_{HSO_4} at 25° and 0° can be approximately calculated from the transference and conductivity data, if it is true that the HSO_4^- ion is present in the sulphuric acid solution in considerable quantity so that its conductivity may enter as a factor. The values obtained are 35—40 at 25°, which are nearly half of that of Δ_{SO_4}, namely, 79 at 25°.

The values of C_H/C have also been calculated from a consideration of the relative effects of sulphuric and hydrochloric acids on the hydrolysis of sucrose at 25° as determined by Ostwald (Abstr., 1885, 882), and on that of ethyl acetate as determined by Kay (*Proc. Roy. Soc. Edin.*, 1898, **22**, 493).

A new isohydric method of determining the hydrogen-ion concentration is described, which consists in determining the relative concentrations of hydrochloric and sulphuric acids which drive back the ionisation of picric acid to the same extent.

The values of C_H/C at various concentrations at 0° and 25° obtained by these different methods are tabulated. In order to derive the concentrations of the HSO_4' and SO_4'' ions from the values of the hydrogen-ion concentration, Noyes and Eastman (*loc. cit.*) assumed that under corresponding conditions the first hydrogen of sulphuric acid is dissociated to an equal extent to that of hydrochloric acid, and

hence estimated the concentration of the non-ionised sulphuric acid. From this concentration and that of the hydrogen ion, the concentrations of the SO_4 and HSO_4 ions were obtained by subtraction. Similar calculations have now been made, and the results show that both the SO_4 and HSO_4 ions are present in large proportions at medium concentrations, that the latter is present in much larger quantity at 0·05 formal and the former at 0·005 formal, and that at 0·05 formal the ratio C_{HSO_4}/C_{SO_4} increases greatly between 0° and 25°. The hydrogen-ion concentration decreases markedly within the same range of temperature.

Experiments have been made on the distribution of sulphuric acid between water and amyl alcohol. The ratio of the concentration of the acid in the alcohol to that in the water was found to increase as the proportion of non-ionised sulphuric acid in the aqueous solution increased. The rate of this increase is somewhat smaller even than in the case of hydrochloric acid, indicating that the non-ionised sulphuric acid is formed from two ions, $H^{\cdot}$ and HSO_4', instead of from three ions, $H^{\cdot}$, $H^{\cdot}$, and SO_4''.

Determinations have been made of the transference of Na, H, and SO_4 during the electrolysis of sodium hydrogen sulphate at 25°. The conductivity of this salt has also been measured at various concentrations at 25°. By combining these data, the concentrations of Na and H ions in a 0·1 formal solution have been calculated, and the values $C_{Na}/C = 0·68$ and $C_H/C = 0·44$ obtained.

From the results obtained by Kay (*loc. cit.*) on the catalysis of ethyl acetate by 0·1 formal sodium hydrogen sulphate, the value of C_H/C has been derived and found to be 0·416.

By means of the values of C_H/C and C_H/C_{Na} derived from the transference and conductivity data, the concentrations of the other ions in a 0·1 formal solution of sodium hydrogen sulphate have been computed, and found to be $C_{HSO_4}/C = 0·44$ and $C_{SO_4}/C = 0·34$ respectively.

From these data, and also from the corresponding data for 0·05 formal sulphuric acid, the values of the product $C_H C_{SO_4}/C_{HSO_4}$, the ionisation constant of the second hydrogen of the acid, have been found to be 0·034 and 0 031 respectively. E. G.

Hydrolysis of Cyanogen. R. NAUMANN (*Zeitsch. Elektrochem.*, 1910, **16**, 772—778).—The conductivity of potassium cyanate solutions is measured; the mobility of the cyanate ion at 18° is 56·5. When cyanogen is passed into aqueous solutions of potassium hydroxide, the conductivity diminishes to a constant value. The observed conductivity agrees well with that calculated on the assumption that cyanide and cyanate are the only products. The conductivity of solutions of cyanic acid at 0° is measured, and the dissociation constant found to be about 120×10^{-6}. When cyanogen is passed through water at 0°, the conductivity increases to a constant value, owing to the formation of cyanic acid (the hydrocyanic acid is practically a non-conductor); the saturated solution contains 0·221 gram-molecule of cyanogen and 0·00005 gram-molecule of cyanic acid per litre, so that 0·023% of the cyanogen is hydrolysed. At the ordinary temperature, the conductivity

of water through which cyanogen is passing depends very much on the rate of the current of gas, and it diminishes rapidly when the gas is stopped. This is due to the decomposition of the cyanic acid into ammonia and carbon dioxide. Cyanogen has, therefore, no definite solubility in water at 18°, the quantity absorbed increasing continuously with the time of contact.

In the calculation of the dissociation constant of hydrocyanic acid (this vol., ii, 386) a serious error was made, the correct value is $\log_{10} K = -29{\cdot}13$ instead of $-10{\cdot}14$. This new value is not in harmony with the view that the *E.M.F.* of the hydrogen-cyanogen element is due to the formation of hydrocyanic acid. T. E.

Electrochemistry of Proteins. II. Dissociation of Basic Caseinogenates of the Alkaline Earths. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, **14**, 601—611. Compare this vol., ii, 679).—It is probable, since the neutral and basic caseinogenates of the alkalis obey Ostwald's dilution law, that a molecule of caseinogenate gives only two ions. The cation is supposed to be a complex ion containing the metal in a non-dissociable form. On this hypothesis basic calcium, strontium, and barium caseinogenates, instead of dissociation into three ions, one of which would be the metal, should give only two complex ions, and the dissociation should obey Ostwald's law.

The solutions examined contained 1 gram of caseinogen to 80×10^{-5} gram-equivalents of calcium, strontium, and barium hydroxide; they were practically neutral to phenolphthalein. The conductivity-dilution curve is in accord with Ostwald's law for a binary electrolyte. If v_1 and v_2 are the ionic velocities and ρ the number of molecules of caseinogenate formed from one molecule of base, the values of $\rho(v_1 + v_2)$ are about twice as great for the caseinogenates of the alkalis as for the alkaline earths. As all the ions concerned are supposed to be complex protein ions, $(v_1 + v_2)$ must be much the same in all the salts. Hence ρ may be taken as two for the alkalis, and one for the alkaline earths. The simplest formula of sodium caseinogenate is $[NaX^{\cdot\cdot} + X(OH)_n'']$, and of calcium caseinogenate,

$$[Ca(X^{\cdot})_2 + \{X(OH)_n'\}_2],$$

each ion having twice as many charges as there are molecules of base per molecule of caseinogen.

The values of $(v_1 + v_2)$ are about 40×10^{-5} at 30°. This is approximately the value calculated by Bredig as the minimum which ionic mobility approaches when the ions become very large. The caseinogenates of the alkalis are nearly completely dissociated, whilst calcium caseinogenate is only 57% dissociated.

The freezing-point determinations of Robertson and Burnett (Abstr., 1909, i, 447) are explainable on the hypothesis that caseinogenate ions are quadrivalent, so that the sodium salt is written:

$$[Na_2X^{\cdot\cdot\cdot\cdot} + X(OH)_n'''']。$$

This formula suggests that two CO_2H groups of the caseinogen molecule are active in the neutralisation of bases. R. J. C.

Influence of the Degree of Dispersity of a Solid Crystal on its Melting Point. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 205—208).—A theoretical paper in which the author analyses

the relationships involved in the transition from the liquid to the amorphous and crystalline solid states of aggregation. H. M. D.

A General Theory for Obtaining Disperse Systems by the Dispersion Method. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 453—474. Compare Abstr, 1909, ii, 132, 221, 306, 606, 646).—A more detailed theoretical discussion of matter already published, and a classification of the methods of peptisation. All the dispersion methods of obtaining disperse systems can be explained according to one general theory, the fundamental general principle of which can be formulated thus: If for some reason or other the intensity of the forces of solution at the surface of disperse particles increases to an extent not greater than that at which the velocity of recrystallisation becomes considerable, then the disperse particles are peptisised by the dispersion medium. For an explanation of the theory, the paper itself must be consulted. Z. K.

Colloidal Chemistry. A General Introduction. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 476—480).—A short historical and theoretical introduction to the two following papers. A good general method of obtaining any solid substance in the state of an amorphous solid solution of any degree of dispersion has been devised, and is based on the rapid cooling of a dilute liquid solution of a substance in a dispersion medium, which, in the pure state itself, solidifies to a glass when rapidly cooled.

The best method of obtaining liquid colloidal solutions is based on the rapid condensation of the molecules of the dissolved substance, when the solvent is replaced by a dispersion medium which dissolves the solvent, but, practically, does not dissolve the dissolved substance. If a concentrated solution is added to such a dispersion medium, fine disperse precipitates are obtained, but not colloidal solutions.

Z. K.

A Simple General Method for Obtaining Solid Colloidal Solutions of any Degree of Dispersion. P. P. VON WEIMARN and J. B. KAGAN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 480—484. Compare preceding abstract).—When a transparent solid solution is heated gradually, the viscosity of the dispersion medium decreases, whilst the velocity of the molecules and molecular aggregates and the coefficient of diffusion increases; consequently, at first, when L in the formula $W = K.(Q-L)/L$ (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 214—228) has not yet increased appreciably, the condensation process occurs, and a bluish-violet opalescence appears, which becomes more and more marked until the solution becomes turbid. When L has increased sufficiently, the dispersion process commences, which is indicated by a diminution in the turbidity of the solution, and by a gradual re-appearance of the bluish-violet opalescence, which then gradually disappears.

When a 0·04% solution of sulphur in alcohol is immersed in liquid air, a solid, strongly opalescent, but partially transparent suspended solution is obtained, which, when heated and well shaken, only shows

the second, the dispersion, process described above. With a 0·02% solution of sulphur a wholly transparent solid solution is obtained, which behaves entirely in accordance with the above theoretical scheme. The solution can be fixed or arrested at any stage of opalescence, or at any degree of dispersion, by rapidly immersing the tube containing the solution at the given stage in liquid air. By employing very dilute solution of sulphur, molecular disperse solid solutions are obtained, in which, when heated, the condensation process is so rapidly followed by the dispersion process that opalescence can sometimes scarcely be observed. Exactly similar results were obtained with phosphorus, sodium bromide, and sodium and potassium chlorides.

A 0·25% solution of phosphorus in alcohol gives a turbid glass; 0·05—0·04% solution yields a partly transparent suspended solid solution, whilst 0·025% gives a wholly transparent suspended solid solution. Z. K.

A Simple Method of Obtaining Sulphur, Selenium, Tellurium, and Phosphorus in a Colloidal State. P. P. von Weimarn and B. V. Maljisheff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 484—487. Compare two preceding abstracts).—Five to twenty-five c.c. of a solution of the metal, saturated at the ordinary temperature or at the boiling point of the solvent (alcohol for sulphur and phosphorus, carbon disulphide for selenium), are rapidly added to 1000 c.c. of the dispersion medium and stirred vigorously. The dispersion medium for sulphur and phosphorus was cold water; for selenium, cold ether. The concentrations of these suspended solutions varied within the limits of several 1/10,000's to several 1/100's%, the solutions in the latter case being very turbid and rapidly coagulating.

The solid solutions are coloured, opalescent, and fairly stable, the stability of the phosphorus and selenium solutions depending on the peptisation processes.

This method of obtaining colloidal solutions is recommended for lecture experiments. The probable solubility of selenium in carbon disulphide is 0·02—0·015 gram in 100 of solvent.

Colloidal tellurium is obtained by adding 0·1 of the element to 5 c.c. of a boiling solution of potassium hydroxide, saturated at the ordinary temperature, and adding the solution of the metal thus formed to 1000 c.c. of cold water, the mixture being stirred vigorously. The stability of the colloidal tellurium solution depends directly on the peptisation processes, and can be greatly increased. The solution can also be made more stable by the addition of gelatin or similar substances. Z. K.

Phenomena of the Colloidal State. Paul Rohland (*Biochem. Zeitsch.*, 1910, **28**, 53—55).—Observations relating to the behaviour of adsorbed substances are referred to as showing that substances in the colloidal condition are frequently much less reactive than they are in the crystalloidal form. The viscosity of colloidal substances is very often increased or decreased by special types of ions.

H. M. D.

The Purification of Colloids by Dialysis. RICHARD ZSIGMONDY and R. HEYER (*Zeitsch. anorg. Chem.*, 1910, **68**, 169—187).—A comparison of parchment, collodion, and fish-bladder membranes in the dialysis of colloidal silica, shows that the last-named acts most rapidly. Collodion membranes, which are perfectly impervious to colloidal silver, allow silica to pass with considerable ease. Continuous renewal of the water in the outer vessel has no advantage over a renewal every two hours. With a suitable membrane, the chlorine is reduced to the limit of recognition by means of silver nitrate in about twenty hours.

An improved dialyser is described, in which a membrane is stretched over a vulcanite ring, placed on a vulcanite tray with edges only 4 mm. high, and provided with radial ribs. The water enters at the centre of this tray, and travels radially in a thin sheet, escaping at the circumference. This appliance allows of rapid dialysis.

In order to estimate chlorine in colloidal solutions of silica, the free hydrochloric acid is first estimated by titration with *N*/100-sodium hydroxide. Another quantity is then exactly neutralised with sodium hydroxide, a drop of 5% potassium chromate solution is added, and the chlorine is titrated with *N*/100-silver nitrate. A standard solution may be used for comparison. Under these conditions, 0·01 c.c. of *N*/100-silver nitrate, run in from a graduated capillary pipette, produces a distinct change of colour, and it is possible to detect 0·004 mg. of chlorine in 1 c.c. of the dialysed liquid. The dialysis, however, proceeds beyond this limit, and it is necessary to employ Jordis' method (this vol., ii, 416) of distillation with sulphuric acid. The residue obtained after neutralising 100 c.c. and evaporating to dryness is transferred to a small distilling flask, 0·5 to 1 c.c. of concentrated sulphuric acid is added after closing the apparatus, and the distillation is continued until nearly all the sulphuric acid has passed over. The chlorine in the absorbing liquid is estimated by Richards' nephelometric method (Abstr., 1904, ii, 287) by means of silver nitrate.

The precipitation of silver chloride is not hindered by the presence of colloidal silica, unless the latter is in very large excess. If some sulphuric acid is present, the precipitation is in all cases normal.

Sodium sulphate is much less readily removed from silica by dialysis than chlorides. Alumina and iron, derived from the sodium silicate used, are not eliminated. Minute quantities of hydrochloric acid increase the stability of the colloid, sodium hydroxide at first diminishes it, but subsequent additions increase the stability.

C. H. D.

The Binary System Pyridine-Potassium Thiocyanate. KARL L. WAGNER and ERNST ZERNER (*Monatsh.*, 1910, **31**, 833—841).—The course of the fusion and solubility curves of two substances between the melting and eutectic points has been thoroughly studied only for the case that the mutual solubilities of the two substances decrease with falling temperature. The temperature-concentration diagram for fusions containing the two substances is then the ordinary curve with two branches, neither of which shows a minimum, and one eutectic point. When the solubility of one substance in the other passes through

a minimum there are four cases which are theoretically possible, and for which the authors give the curves. One of these is where the two branches of the fusion curve intersect below the minimum in an eutectic point. The system pyridine–potassium thiocyanate partly conforms to this type, differing from it in that between the eutectic point and the melting point of the potassium thiocyanate there is a four-phase invariant system, namely, liquid pyridine–liquid potassium thiocyanate–solid potassium thiocyanate–vapour. The mutual solubility of the two liquid phases increases as the temperature falls.

The various points on the curves were obtained by heating together weighed quantities of pyridine and potassium thiocyanate in sealed tubes, and observing the temperature at which the crystals disappear or are deposited.

The eutectic temperature is approximately $-43·3°$, the mixture containing 3·1% of potassium thiocyanate. The four-phase system is formed at 188·5°.

Potassium thiocyanate has m. p. 173·8°. T. S. P.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IV. Phenol and the Methylcarbamides. ROBERT KREMANN [with J. DAIMER, F. GUGL, and H. LIEB] (*Monatsh.*, 1910, **31**, 843—853. Compare Abstr., 1907, i, 912).—The melting-point curve for mixtures of phenol and *as*-dimethylcarbamide falls from the melting point of the dimethylcarbamide to a break at 25—25·5°, and then to a eutectic point at 9°, representing mixtures containing 63% and 84% of phenol respectively. The break at 25° is due to the separation of the compound formed from one molecule of each of the components, the composition of the compound being determined by measuring the times of arrest for mixtures varying in composition from 0—63% phenol. The eutectic is a mixture of this compound with phenol.

The curve obtained for mixtures of phenol and monomethylcarbamide is similar in character, the break occurring at 8° and the eutectic at $-7°$ representing mixtures containing 60% and 77% of phenol respectively. The break at 8° is again due to the separation of a compound containing one molecule of each of the components.

The curve for mixtures of phenol and *s*-dimethylcarbamide is the ordinary one for a two-component system giving one compound and two eutectics. The compound is formed from two molecules of phenol and one molecule of dimethylcarbamide, and has m. p. 14°. The eutectic temperatures are $+5°$ and $-3°$, representing mixtures containing 81% and 47% of phenol respectively.

The above results support the statement that asymmetric substitution diminishes the power to form compounds, whereas symmetrical substitution does not have this effect (compare Abstr., 1906, ii, 268).

T. S. P.

Equilibrium between Solid Cuprous Iodide and Aqueous Solutions Containing Cupric Salt and Iodine. WILLIAM C. BRAY and G. M. J. MACKAY (*J. Amer. Chem. Soc.*, 1910, **32**, 1207—1214).—The results described in this paper are the outcome of a study of the law of the mass-action in dilute aqueous solutions.

Cuprous iodide is only slightly soluble in water, but in the presence of iodine a considerable amount dissolves, owing to the formation of cupric iodide and tri-iodide. The following equilibria are involved: $CuI(solid) + \frac{1}{2}I_2 = Cu^{\cdot\cdot} + 2I'$ and $I_3' = I_2 + I'$.

Values have been determined at 25° under widely different conditions for the former equilibrium. The ionic concentrations in the various mixtures were calculated by means of the relations derived from conductivity measurements. The values obtained for the equilibrium function $K' = (Cu^{\cdot\cdot})(I')^2/I_2^{\frac{1}{2}}$ show that this equilibrium conforms with the law of mass-action only as far as the influence of iodine is concerned and deviates from it when cupric salt, iodide, or other salt is added. In all cases, however, the deviations are of such a nature that K' increases with increasing concentration. This result is an illustration of the rule that when the concentration of an ion is based on conductivity measurements, the ratio of its "activity" (Lewis, Abstr., 1908, ii, 16) to its concentration decreases somewhat with increasing ion concentration. From this rule it follows that the solubility product of a salt will not be constant, but will increase with increasing ion concentration.

Values have also been calculated for the equilibrium function, $K = (I')(I_2)/(I_3')$. The results confirm the conclusion (this vol., ii, 820) that K decreases with increasing concentration of iodide, but that other salts do not produce a similar effect.

Conductivity determinations made with several of the equilibrium solutions have shown that cupric iodide and tri-iodide are ionised to the same extent as magnesium chloride, and that cupric nitrate is ionised to a somewhat smaller extent. E. G.

Equilibria in the Precipitation of Metals by Hydrogen Sulphide. LUDWIK BRUNER and J. ZAWADSKI (*Bull. Acad. Sci. Cracow*, 1909, 267—312).—The precipitation of thallium sulphide by hydrogen sulphide is a reversible reaction. Measurements in solutions of different acid and hydrogen sulphide concentrations show that at 25°, $K = [Tl^{\cdot}]^2[H_2S]/[H^{\cdot}]^2 = 0{\cdot}637$. The equilibrium has also been approached from the other side by adding thallium sulphide to sulphuric acid and passing hydrogen sulphide. Measurements at 0° and 40° lead to values for the equilibrium constant from which a value for the heat of precipitation of thallium sulphide is obtained by van't Hoff's equation, in agreement with that derived from thermochemical data.

The values of K obtained for the precipitation of ferrous sulphide vary, owing to experimental difficulties, but lie between $2{\cdot}7 \times 10^3$ and $9{\cdot}1 \times 10^3$. Calculations are made of the solubility products of iron, cadmium, and lead, and the results of previous observers for these and other sulphides are discussed and criticised. It is shown that the published values for the solubility of sulphides in pure water, calculated from the electrical conductivity, are not in accordance with the analytical behaviour of the metals.

The results from thallium sulphide are employed to calculate the electrolytic potential of sulphur. The experiments with lead sulphide lead to a result in close agreement with this. From the potential thus

obtained, the solubility products of the sulphides are calculated by means of Bodländer's formula, and values are obtained in good agreement with the experimental results, with a few exceptions. The observed solubilities are then used to calculate the heat of formation of the sulphides, in good agreement with Thomsen's results.

C. H. D.

Equilibria in the Precipitation of Metals by Hydrogen Sulphide. LUDWIK BRUNER and J. ZAWADSKI (*Zeitsch. anorg. Chem.*, 1910, **67**, 454—455).—Owing to differences in the methods of expressing concentrations in the data from different sources, there are certain numerical errors in the authors' calculations (see preceding abstract). The corrected value for the potential of sulphur against the hydrogen electrode is $E_h = +0{\cdot}545$. Employing this value to calculate the solubility constants, and adopting more recent values for the electrolytic potentials of iron and silver, the agreement between the calculated and observed values is improved. The imperfect agreement in the case of zinc is attributed to the known transformation of βZnS into the less soluble αZnS. C. H. D.

Equilibria in the Action of Potassium Hydroxide on Mercuric Bromide and Chloride. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **68**, 165—168).—In the reaction: $HgBr_2 + 2KOH \rightleftarrows HgO + 2KBr + H_2O$, the constant $[HgBr_2][KOH]^2/[KBr]^2$ is found to have the average value $10{\cdot}1 \times 10^{-4}$. Basic salts are, however, also formed. The reaction of potassium bromide with an excess of mercuric oxide (Bersch, Abstr., 1891, 1413; Bugarszky, Abstr., 1893, ii, 450, 566) gives a constant 15×10^{-4}.

The precipitation of mercuric chloride by an excess of potassium hydroxide has also been measured in two concentrations. C. H. D.

Kinetics of the Formation of Ethyl Ether from Alcohol and Ethyl Hydrogen Sulphate. ROBERT KREMANN (*Monatsh.*, 1910, **31**, 671—685).—The rate at which the reaction between ethyl alcohol and ethyl hydrogen sulphate proceeds at 100°, 125°, and 135° has been determined by measuring the increase in acidity during the course of the reaction. The increase in acidity is not a direct measure of the extent to which the reaction has taken place, since the sulphuric acid formed enters into reaction with the alcohol to re-form ethyl hydrogen sulphate according to the equilibrium reaction: $EtOH + H_2SO_4 \rightleftarrows EtSO_4H + H_2O$. At the temperature of experiment this equilibrium adjusts itself practically instantaneously, and since the equilibrium constant has been previously determined (this vol., ii, 700), the correction to be applied to the observed increase in acidity in order to obtain a correct measure of the velocity of reaction can be determined.

The alcohol was always in large excess, and the reaction is assumed to be bimolecular, a number of simplifications having to be made in order to reduce the differential equation to a form in which it can be readily integrated.

The values obtained for the velocity constant are not even approximately constant, but decrease very considerably during the

course of the reaction, the rate of decrease being the greater the greater the initial concentration of the ethyl hydrogen sulphate. This is probably due to the retarding effect of the water formed by the action of the alcohol on the sulphuric acid.

A comparison of the times necessary for the reaction to proceed to the same extent at different temperatures gives a temperature quotient of 2·5 for 10°.

The ordinary method for making ether is discussed in the light of the results obtained. T. S. P.

The Mechanical Vibration of Atoms. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], 20, 657—660).—On the assumption that the atoms of an element may be replaced by cubes of uniform density, having the same mass as the atoms, and just large enough to circumscribe them, the author calculates the wave-lengths corresponding with the fundamental mechanical vibrations of the atoms of the alkali metals and the halogens. It is shown that the wave-lengths corresponding with the vibration of the molecules of the alkali halogen salts are probably represented by the sums of the wave-lengths of the constituent elements. When the computed wave-lengths for sodium chloride, potassium chloride, bromide and iodide are compared with the lengths of the longest infra-red waves examined by Rubens and Hollnagel in the case of these four substances, it is found that a nearly constant ratio of eight is obtained. According to this, the calculated mechanical period of vibration is only three octaves below the lowest period experimentally investigated in each of these four cases. H. M. D.

New Proof of the Existence of Molecules. THE SVEDBERG and NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1910, 74, 513—536. Compare Abstr., 1909, ii, 277, 561, 723).—The relationship between the absorption in a colloidal solution and the size of the particles has been further investigated. Some of the measurements were made with a Vierordt spectrophotometer and a light source giving a continuous spectrum, but the later and more accurate measurements were made with a König-Martens spectrophotometer with homogeneous light. The results are expressed in terms of $k = \frac{1}{d \log_e} \log \frac{I_0}{I}$ or $k_m = k/\text{mol.}$ per litre, where I_0 and I represent the intensities of the light before and after traversing the absorbing layer, and d is the thickness of the absorbing layer in cm.

A series of solutions of colloidal gold containing particles of different magnitude have been prepared, and it is shown that the wave-length for maximum absorption diminishes progressively as the size of the particles diminishes, whilst the maximum value of k_m increases at first, attains a maximum, and finally diminishes with progressive diminution in the size of the particles. When a solution of phosphorus in ether is added to a solution of chlorauric acid, $HAuCl_4$ (the absorption maximum of which is in the ultra-violet), the absorption spectrum is at first displaced a little towards the ultra-violet, and then a slow continuous displacement towards the visible spectrum occurs. The

change from gold solutions with a known degree of dispersion (size of particle) and absorption in the visible region to chlorauric acid (with molecular dispersion and maximum absorption in the ultra-violet) is continuous.

Examination of solutions of colloidal and dissolved selenium confirms the above results; in this case the maximum absorption of the molecular solution (in carbon disulphide) lies in the visible region. Some observations with indigotin solutions are also described.

A relationship has been found between the absorption exerted by each particle and the degree of dispersion. G. S.

Berzelius' Error as to the Discoverer of the Law of Neutralisation. MAX SPETER (*J. pr. Chem.*, 1910, [ii], 397—408).—Historical. C. S.

A Simplified and Improved Form of Toepler's Mercury Air-Pump. ANDREAS VON ANTROPOFF (*Chem. Zeit.*, 1910, **34**, 979).—The throwing up of mercury in the Toepler pump is avoided in this form by placing the cylindrical vessel in an inclined position. The vessel need not have a capacity of more than 100 c.c. It is drawn out into a conical form at its upper end, at the junction with the capillary. The pump may be worked rapidly without injury, and is very simple in construction. C. H. D.

New Modification of the Kipp Gas Generator. F. ALEX. McDERMOTT (*J. Ind. and Eng. Chem.*, 1909, **1**, 811—812).—The paper contains a sketch and description of a modification of the Kipp gas generator, in which the base is made cylindrical with a dome-shaped top and in two portions, which fit together with a ground joint; an indentation encircles the inside of the cylinder at a convenient distance from the bottom, and carries a perforated porcelain or lead tray to carry the active material; it has a hole in the centre through which the stem of the acid reservoir passes in the usual manner.

The advantages claimed for this apparatus are: (1) accessibility of all parts for cleaning and recharging; (2) stability, as it is not so tall as the usual forms; (3) an even distribution of the active material over a relatively large area. F. M. G. M.

Weighing. OTTO KUHN (*Chem. Zeit.*, 1910, **34**, 1097—1098, 1108—1109).—Neglect to reduce the weighings of crucibles and other chemical apparatus to the weight in a vacuum may cause an error of several tenths of a milligram if the atmospheric conditions vary between two weighings. The correction should therefore be made in analytical work. Double weighing should be employed in order to eliminate errors due to unequal expansion of the arms of the balance. C. H. D.

Inorganic Chemistry.

The Molecular Weight of Water in Different Solvents. GIUSEPPE BRUNI and M. AMADORI (*Gazzetta*, 1910, **40** ii, 1—8).—Water is not sufficiently soluble in any hydrocarbon to permit of cryoscopic measurements, but a number of other solvents which might be expected to cause association have been examined. In each case the degree of association increases with the concentration, being very near to 1 in dilute solutions in bromoform, ethylene bromide, dimethylaniline, *p*-toluidine, methyl oxalate, methyl succinate, and veratrole. Alcohol, phenol, and acetic acid are associated in the same solvents, ethylene bromide having the greatest effect and methyl succinate the least. Alcohol and phenol, like water, form single molecules in dilute solution, but acetic acid is associated even in very dilute solution in ethylene bromide. C. H. D.

Direct Synthesis of Volatile Hydrogen Compounds. ALEXANDER CH. VOURNASOS (*Ber.*, 1910, **43**, 2272—2274).—Not only can phosphorus, arsenic, antimony, and sulphur be transformed into their hydrides by heating with sodium formate, but also other elements, especially those which are volatile, and various compounds. The less volatile a substance is, the more difficult it is to reduce it.

If a compound is made up of two volatile components, both are reduced, giving the two hydrides; this is the case with the sulphides of phosphorus, arsenic, and antimony, and the phosphides of arsenic and antimony. If only one component is volatile, that alone is hydrogenised; for example, the phosphides, sulphides, arsenides, antimonides, selenides, and tellurides of the metals. A large number of chloro-, bromo-, iodo-, and fluoro-derivatives, especially those of the heavy metals, give the corresponding halogen hydrides. Nitrides of the metals give ammonia. Silicides, borides, and carbides are not reducible.

Selenium and tellurium form the hydrides when heated with sodium formate to 400°; the yield is limited, owing to the reverse reaction (decomposition) which takes place.

Hydrogen silicide is formed to a slight extent when an equimolecular mixture of amorphous silicon and sodium formate is heated at 1300°. The reaction takes place more readily when the silicon is dissolved in aluminium (2 parts of silicon to 60 of aluminium) and the temperature kept at 750°. Hydrogen boride is formed when the silicon is replaced by amorphous boron (1 part of boron to 25 parts of aluminium); it also results when a mixture of boron with sodium formate is heated in the electric arc. T. S. P.

Some Analogies between Derivatives of Oxygen and Nitrogen. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 94—101. Compare this vol., ii, 844).—The author amplifies and

extends the views put forward in the former paper as to the analogy displayed in many of their reactions between hydrogen peroxide, hydroxylamine, hydrazine, etc. R. V. S.

Decomposition of Ozone by Ultra-violet Light. EVA VON BAHR (*Ann. Physik*, 1910, [iv], **33**, 598—606).—When ultra-violet light from a quartz-mercury lamp is allowed to fall on ozonised oxygen, the ozone is decomposed. The rate of decomposition increases rapidly as the pressure on the gas is reduced. For a given intensity of the incident ultra-violet radiation, the ozone disappears at a rate which agrees with the requirements of the equation for a unimolecular change, if the pressure is kept constant. The velocity constant is nearly independent of the pressure when this exceeds 200 mm. of mercury, but for lower pressures the constant increases rapidly as the pressure falls.

In consequence of the decomposing action of ultra-violet light, the measurement of the absorption of ultra-violet radiation cannot be applied to the estimation of ozone at low temperatures. H. M. D.

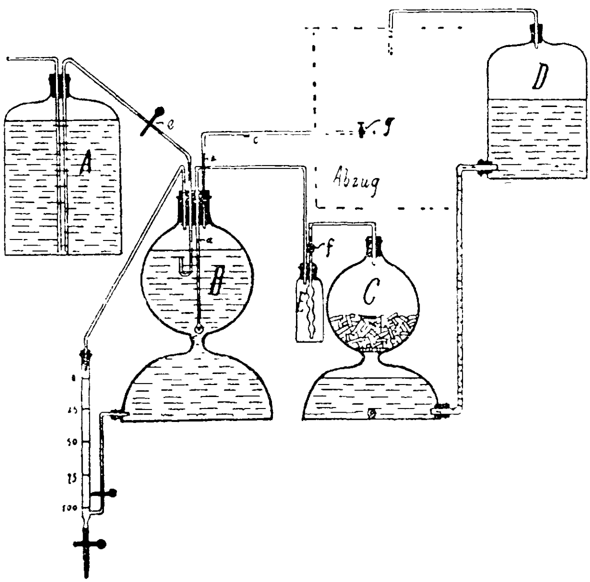
Ozone. V. The Development of Heat in the Decomposition of Ozone. ANTON KAILAN and STEPHAN JAHN (*Zeitsch. anorg. Chem.*, 1910, **68**, 243—250. Compare Abstr., 1909, ii, 37).—The oxygen, containing 10% of ozone, is led through a decomposition tube containing soda-lime, enclosed in a vacuum vessel as calorimeter containing water. A manganin spiral is also provided for heating the apparatus electrically in order to calibrate it. With this apparatus, a rise of temperature of 0·2° in ten to fifteen minutes may be measured to 0·001°. The corrected value for the development of heat in the decomposition of ozone at constant volume is 34,500 cal. per gram-molecule.

Experiments with other catalytic agents show that platinum-black gives high values, and rapidly loses its activity. With a heated platinum wire, which is easily calibrated, the concordant value 34,000 cal. per gram-molecule is obtained. C. H. D.

New Hydrogen Sulphide Apparatus. STEFAN URBASCH (*Chem. Zeit.*, 1910, **34**, 1040—1041).—The apparatus may be used in the laboratory room close to a fume chamber without causing any inconvenience whatever, and, owing to the high pressure, several solutions may be treated simultaneously with hydrogen sulphide.

A holds 5 litres, *B* altogether 6 litres, *C* altogether 4 litres, *D* also 4 litres. When used for the first time, *B* is filled with water, and a glass tube reaching to the bottom is introduced. *C* contains iron sulphide, *D* dilute hydrochloric acid (2 : 1). Hydrogen sulphide is now passed until the water in *B* is quite saturated, and the apparatus is then fitted up as shown in the figure. If the gas is wanted first, stopcock *f* and then stopcock *g* are opened, causing the acid to flow from *D* to *C*. The gas evolved enters by the tube *a* into *B*, passes through the water, and by means of the tube *b c* and stopcock *g* then passes through the solution to be tested. The gas current is easily regulated, and the spent acid is drawn off from the bottom of *C*. If saturated

hydrogen sulphide water is required, it is allowed to drain from the burette, and the volume may thus be measured. Owing to the difference in level, fresh water flows from *A* into *B* until the former height has been again reached, and this water becomes again saturated with hydrogen sulphide. Not until 5 litres of hydrogen sulphide water have been used is there any need for replenishing the contents of *A*. During the passing of the gas, the siphon is closed, as otherwise a little of the solution might find its way into *A*. When no gas but only the solution is required,



no fresh water is introduced into *B*; the contents last a long time and cannot deteriorate. In order to empty the burette when the siphon is closed, it is necessary to open the pinchcock *f* for a momont. *B* is made of dark glass so as to prevent any decomposition by light.

L. DE K.

The Constitution of Weber's Acid. KONRAD W. JURISCH (*Chem. Zeit.*, 1910, **34**, 1065—1066).—Objections are brought forward against the validity of the ordinary structural formulæ for sulphuric acid and nitrosylsulphonic acid. The former is regarded as an additive compound of sulphur trioxide and water, and the latter as

$$H_2O,SO_3,SO_3,N_2O_3.$$

Thermochemical reasons are given for supposing that the group SO_3 is present in both compounds, and that hydroxyl groups are absent.

C. H. D.

Action of Crushed Quartz on Nitrate Solutions. HARRISON E. PATTEN (*J. Physical Chem.*, 1910, **14**, 612—619).—A filter bed was made with fine quartz flour of 740 sq. cm. area per gram, which was

washed with hydrochloric acid and distilled water. On percolating through it an 0·01*N*-solution of silver nitrate sterilised with chloroform, some silver remained on the quartz in an insoluble condition, and the filtrate contained upwards of 1% of nitrite calculated as silver nitrite. The silver remaining on the quartz, which was perhaps in the form of silver oxide or silver silicate, was soluble in ammonia, but the percolated silver nitrate was not tested for acidity.

The reduction of nitrate decreases as the adsorptive capacity of the quartz surface becomes satisfied. Sodium nitrate under sterile conditions is not reduced in contact with quartz to give any substance oxidisable with permanganate. The looser combination and the greater hydrolysis of the heavy metal nitrates may facilitate their reduction by quartz. R. J. C.

The Hydration of Metaphosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1910, **68**, 266—268. Compare this vol., ii, 607).—Although it is not found possible, on account of the volatility of metaphosphoric acid, to reach the temperature at which orthophosphoric acid would pass directly into the meta-acid, it is found that metaphosphoric acid in aqueous solution becomes directly hydrated to form the ortho-acid, without any intermediate formation of pyrophosphoric acid. C. H. D.

Synthesis of Hydrogen Arsenide from its Elements. ALEXANDER CH. VOURNASOS (*Ber.*, 1910, **43**, 2264—2272).—Dry nascent hydrogen, as prepared by heating sodium formate, readily combines with certain of the metalloids to form the hydrides of these elements (compare this vol., ii, 286). Hydrogen arsenide may be obtained by passing the vapours of arsenic heated to 460° over sodium formate contained in a tube heated to a temperature just below the decomposition point of the formate. The heat of the arsenic vapour completes the decomposition, and a mixture of hydrogen and hydrogen arsenide is obtained. The reaction is carried out much more conveniently by heating a mixture of three parts of powdered arsenic with eight parts of dry sodium formate rapidly to 400° in a round-bottomed flask. Yields of 12—17 volume % of hydrogen arsenide have been obtained.

Instead of using sodium formate alone, it is better to use an equimolecular mixture of sodium formate and sodium hydroxide or lime to prepare the nascent hydrogen, as this prevents the formation of sodium oxalate, and hence of carbon monoxide, when the temperature is raised too high. Moreover, arsenious oxide, sodium arsenite, or arsenic acid may be used in place of arsenic. When a mixture of equal weights of sodium formate and normal sodium ortho-arsenite is heated to temperatures not exceeding 400°, a gaseous mixture of hydrogen arsenide and hydrogen is obtained containing not more than 2—3% of the latter gas.

One great advantage of this reaction is that sulphur compounds and other inorganic and organic compounds of arsenic, for example, solid hydrogen arsenide, Schweinfurt green, arsenic trisulphide, arsenic-containing magenta, etc., all give arsenic trihydride when heated with

sodium formate, or with a mixture of sodium formate and sodium hydroxide. Marsh's test may thus be carried out without it being necessary to transform the arsenic compound into one of its oxygen derivatives. Organic compounds are best destroyed by oxidation with nitric and sulphuric acids, and the dry residue, which may still contain carbon, heated directly with the formate mixture. In some cases, it is an advantage to transform the arsenic acid produced by the oxidation into arsenic sulphide before further treatment. This is best done by means of pure hydrogen sulphide prepared by heating ten parts of the formate-hydroxide mixture with three parts of flowers of sulphur to 400°.

Urine which is to be tested for arsenic is made strongly alkaline and evaporated to dryness, the residue then being treated as above. Acids are first neutralised, and then evaporated, etc. Aniline dyes and textiles dyed with colours containing arsenic can be treated directly with the formate-hydroxide mixture, since organic matter does not affect the reaction, but it is better first to isolate the arsenic as chloride by distillation, and then transform it into the sulphide, or else to destroy the organic matter by fusion with sodium nitrate.

By the above methods it is possible to detect 0·001 mg. of arsenic.

A mixture of antimony oxide and sodium formate gives no trace of hydrogen antimonide when heated to 400°, metallic antimony alone being formed. When, however, sodium antimonite is used instead of antimony oxide, and the mixture rapidly heated to 800°, small quantities of the hydride of antimony are formed. This compound is also produced to a slight extent when metallic antimony is used and the mixture heated to a bright red heat. Antimony tri- and penta-sulphides simply give rise to metallic antimony and hydrogen sulphide at 400°. Thus arsenic may be separated from antimony in their compounds by heating with the formate-hydroxide mixture to 400°, the antimony remaining behind in the metallic form. At 800°, however, some antimony also volatilises as the hydride. T. S. P.

Percarbonates. ERNST H. RIESENFELD (*Ber.*, 1910, **43**, 2594—2595).—Polemical. A reply to Tanatar (compare this vol., ii, 33, 203, 290, 774). T. S. P.

Silicon Monosulphide. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 294—300).—When silicon (in the form of ferro-silicon) and sulphur are heated together in an electric arc furnace, a vigorous reaction takes place, and a grey mass results, from which, by sublimation in an electric furnace, silicon monosulphide may be obtained. The compound sublimes at 940—980° at 20—30 mm., and it occurs in two forms, namely, a black solid which may assume a vitreous character, and a yellow powder. On resublimation of either form, both are produced, the yellow one being deposited in the colder parts of the tube employed. Analysis of either product leads to the formula SiS, and the substance does not appear to be a mixture. The black modification has D_4^{15} 1·853. With alkalis, the compound reacts according to the equation $SiS + 2KOH = SiO_2 + K_2S + H_2$. The black sulphide dissolves in water with evolution of hydrogen sulphide and

formation of soluble silica, and of a finely-divided orange substance, which appears to be related to the oxygenated silicon hydrides of Wöhler (*Annalen*, 1863, **127**, 257). It decomposes slowly in water, more rapidly in alkalis, with evolution of hydrogen and formation of silica. It dissolves in hydrofluoric acid, hydrogen being evolved, but it is insoluble in other acids. The yellow sulphide is also hydrolysed with evolution of hydrogen sulphide, but instead of soluble silica and the compound just described, a white, insoluble substance is formed, which yields hydrogen when treated with alkalis.

R. V. S.

The Equilibrium Diagram of the Silver–Cadmium Alloys. GIUSEPPE BRUNI and E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, **68**, 198—206).—Silver and cadmium are melted together in an atmosphere of nitrogen. The diagram obtained is simpler than that of Rose (Abstr., 1905, ii, 86), although agreeing with it in the form of the liquidus. From 0 to 80 atomic % of cadmium, the alloys form a continuous series of solid solutions. The crystallisation intervals increase from 0 to 40 atomic % Cd, diminish to zero at 50%, increase to 60%, and again reach zero at 80% Cd. This indicates the existence of two compounds, AgCd and $AgCd_4$, both of which form solid solutions. This part of the curve resembles that of the magnesium–cadmium alloys (Grube, Abstr., 1906, ii, 355). The compound AgCd undergoes a transformation at 433°.

From 80 atomic % Cd to 97%, crystals of $AgCd_4$ separate, and from this point onwards solid solutions are formed. There is no eutectic point, the freezing point of cadmium being raised by the addition of silver, even in minute proportion.

C. H. D.

Peptisation of Silver Bromide. RAPHAEL E. LIESEGANG (*Zeitsch. Photochem.*, 1910, **9**, 60—64).—A theoretical paper in which the author discusses the nature of the changes involved in the granulation and peptisation of the silver haloids.

H. M. D.

Silver Nitrate Formed by the Action of Nitric Acid on Silver Sulphide. HIPPOLYTE GRUENER (*J. Amer. Chem. Soc.*, 1910, **32**, 1030—1032).—Boiling nitric acid of concentration above 5% dissolves silver sulphide rapidly, forming silver sulphate and nitrate. Acid stronger than 94%, however, forms only the sulphate. The maximum amount of nitrate (95%) is obtained by the use of 15—20% acid, greater dilution than this resulting in a smaller percentage. The production of the nitrate is diminished by boiling the acid or prolonging its time of action.

W. O. W.

Action of Potassium Hydroxide on Normal Calcium Phosphate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 662—664).—Normal calcium phosphate is not acted on when heated with a large excess of potassium hydroxide at 96—97° for fifty hours.

T. S. P.

The Binary Systems of Calcium Metasilicate with Calcium Chloride and Calcium Fluoride. B. KARANDÉEFF (*Zeitsch. anorg. Chem.*, 1910, **68**, 188—197).—Mixtures of calcium carbonate, silica, and calcium fluoride are melted in a carbon tube and subjected to thermal analysis, the porcelain tube of the thermo-couple being protected with a layer of tar and graphite. Calcium metasilicate and calcium fluoride form a simple eutectiferous series, with a eutectic point at 48 molecular % CaF_2 and 1130°. The conversion of pseudowollastonite into wollastonite on cooling may be followed microscopically, but does not produce any thermal effect.

The eutectic point in mixtures of calcium metasilicate and calcium chloride lies close to the calcium chloride point, and 8° below it. Solid solutions may be formed up to 10 molecular % $CaCl_2$. There is no evidence of the formation of additive compounds. C. H. D.

Metallic Strontium. BEN L. GLASCOCK (*J. Amer. Chem. Soc.*, 1910, **32**, 1222—1230).—A study has been made of the conditions necessary for the preparation of strontium by the electrolysis of its fused chloride. A quantity of the metal was prepared in the following manner. A hemispherical, cast-iron vessel of 25 cm. diameter was used as a container, and a carbon anode 8 cm. × 8 cm. was employed. With pure strontium chloride as electrolyte, and a current of 125 amperes and 40 volts for seven hours, 76 grams of strontium were obtained, giving a current efficiency of 5·3%. The metal thus obtained had a purity of 97—98·5%, D 2·55, and specific heat 0·0742.

Strontium is a very light, soft metal, which has a silvery lustre when freshly cut, but rapidly becomes yellow and afterwards coated with a white layer of oxide. It reacts with water, methyl, and ethyl alcohols, ethyl acetoacetate and malonate, and aniline with evolution of hydrogen, and also reacts slowly with boiling ethyl iodide. The metal is without action on silicon tetrachloride. It dissolves readily in liquid ammonia, forming a deep blue solution from which a dark blue precipitate separates. It burns in an atmosphere of carbon dioxide and illuminating gas as energetically as in air, but not so violently as calcium does under similar conditions. When hydrogen and nitrogen are passed over the heated metal, the hydride and nitride are formed. An alloy of strontium and iron has been prepared and is described. E. G.

The Ternary Alloys of Magnesium, Zinc, and Cadmium. I. GIUSEPPE BRUNI, G. SANDONNINI, and E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, **68**, 73—90).—Magnesium and zinc form a single compound, $MgZn_2$, and no solid solutions. On the other hand, zinc and cadmium form a simple eutectiferous series, whilst magnesium and cadmium form a compound, MgCd, which forms a continuous series of solid solutions with both components. It is found that the system $MgZn_2$–Cd behaves like a binary system, and the present investigation includes the alloys of the ternary group $MgZn_2$–Cd–Zn, leaving the remainder for a second part.

In the zinc-cadmium series, the eutectic point is at 262° and 73·5 atomic % Cd, and cadmium holds about 3 atomic % Zn in solid

solution. The eutectic point between Zn and $MgZn_2$ lies at 363° and 7 5 atomic % Mg. The eutectic point Cd–$MgZn_2$ lies at 280° and 80·05 atomic % Cd.

The ternary series examined is therefore of a simple type, having three binary eutectic lines and a ternary eutectic point, the last lying at 250° and 73 atomic % Cd, 25% Zn, and 2% Mg.

The total number of alloys examined in this section of the system is 109. C. H. D.

Chemical Analyses of Minoan Metals from the Excavations of Crete. ANGELO MOSSO (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 225—228).—Of six samples of lead of Minoan origin only one contained tin (1·460%). It is suggested that the absence of tin objects in the Minoan remains is to be ascribed to the action of the "tin pest." A piece of gold was found to be alloyed with 20% of silver, this alloy being the so-called electron. A piece of silver was found to contain 20% of copper. The two pieces of electron and the piece of silver analysed belong to the third Middle Minoan Period (Evans' classification). A sphere of mineral examined was found to be an emery of the composition:

Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SiO_2.	Total.
55·40	38·60	1·50	0·54	3·70	99·74

R. V. S.

Antique Glass Mirror. FRANZ W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1910, **31**, 781—784).—Chemical investigation of an antique glass mirror found in a large Roman grave-yard in the Wiener Strasse in Laibach shows that it was made by pressing lead foil on to the glass, some kind of balsam being used as an adhesive. In the course of centuries the balsam has resinified and entered into combination with the lead, the lead thereby being converted for the most part into red lead. The lead forming the frame and hinder part of the mirror was changed on the surface into the basic carbonate. T. S. P.

The Influence of Light on White Lead Blackened by Hydrogen Sulphide. ERNST TÄUBER (*Chem. Zeit.*, 1910, **34**, 1126).—Contrary to the results of Sacher (this vol., ii, 712), the author finds that lead sulphide in white lead paints is bleached by the action of light, even in the absence of oxygen. The action is attributed to the peroxides of the drying oils in the paints. A blackened surface of white lead, coated in places with poppy-seed oil, is bleached by light only in the parts coated with oil. Freshly painted surfaces are even bleached in the absence of light, although more slowly. C. H. D.

Crystallisation of Fused Lead Silicates. SIEGFRIED HILPERT and RICHARD NACKEN (*Ber.*, 1910, **43**, 2565—2573. Compare Abstr., 1909, ii, 890).—The authors describe various apparatus by means of which they have taken the cooling curves of fused mixtures of lead oxide and silica, the fused mass being vigorously stirred during the cooling, and have measured the velocity of crystallisation and the crystallisation power (number of nuclei formed) of such fusions at

different temperatures. The results obtained are combined in a freezing-point diagram for mixtures varying in composition from lead monoxide to lead metasilicate. At first sight the curve seems to comprise two eutectics and one maximum, the latter corresponding with lead orthosilicate, m. p. 740°. The eutectics, however, correspond with the compositions $3PbO,2SiO_2$ and $3PbO,SiO_2$, and further careful experiments (cooling curves, measurements of velocity of crystallisation, and microscopic examination of thin sections) with mixtures of these compositions show that the first supposed eutectic really consists of two eutectics close together, with a small maximum in between, corresponding with the compound $3PbO,2SiO_2$, m. p. about 690°. The evidence for the second compound, $3PbO,SiO_2$, is not so satisfactory, but the examination of thin sections points to its existence.

T. S. P.

Ternary Alloys of Copper, Antimony, and Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 197—201, 243—247. Compare this vol., ii, 779, 852).—The first paper contains the experimental results obtained for the ternary systems Cu_3Sb–Sb–Bi, and the diagram of the system constructed with their aid.

In the second this diagram is discussed. Microscopic examination of the alloys has confirmed the results obtained by thermal methods, and photomicrographs of some of the typical appearances observed are reproduced in this paper. R. V. S.

Compounds of Nitric Oxide with Cupric Salts. WILHELM MANCHOT (*Annalen*, 1910, 375, 308—315. Compare Kohlschütter, Abstr., 1904, ii, 734; Manchot, this vol., ii, 137). It has long been known that a solution of copper sulphate in concentrated sulphuric acid develops a violet or bluish-violet coloration with nitric oxide. The author shows that the coloration is due to the formation of an easily dissociable compound of 1 mol. each of copper sulphate and of nitric oxide. Its formation is influenced by the concentration of the water and of the copper salt present. No coloration or absorption of nitric oxide can be detected when sulphuric acid containing less than 70·8% of H_2SO_4 is used, whatever the concentration of the copper sulphate. At 0° and 752 mm., solutions containing 0·0053 to 0·0265 mol. of $CuSO_4$ per litre of 97·6% sulphuric acid absorb exactly 1 mol. of nitric oxide per 1 atom of copper; with greater concentrations of copper sulphate the amount of nitric oxide absorbed is less. A solution containing about 0·0175 mol. of $CuSO_4$ absorbs only 1 mol. of nitric oxide per 1 atom of copper when the pressure of the nitric oxide is increased from 322 mm. to 1303 mm.

Similar results are recorded for alcoholic solutions of hydrated cupric chloride. The dark violet compound is even more sensitive than the preceding to the decomposing action of water, for even in absolute alcohol solutions containing 0·005 to 0·1352 mol. of $CuCl_2$ per litre absorb only 17 to 18 litres of nitric oxide (at 0° and 750—753 mm.) per 1 atom of copper.

When dry hydrogen chloride is led into liquid nitric oxide cooled by liquid air, or when nitric oxide is passed into liquid hydrogen chloride, a dark red liquid is formed, which rapidly solidifies to a dark red, crystalline mass; the substance decomposes, however, even at the temperature of a mixture of solid carbon dioxide and acetone.

C. S.

Atomic Weight of Mercury. II. C. W. EASLEY (*J. Amer. Chem. Soc.*, 1910, **32**, 1117—1126).—In an earlier paper (Abstr., 1909, ii, 1013), the atomic weight of mercury was determined by a study of the ratio $HgCl_2 : 2AgCl$. In order to confirm the value thus obtained, estimations were made of the mercury in mercuric chloride by precipitating mercuric oxide with sodium hydroxide and reducing it by means of hydrogen peroxide. Although the results of these experiments agreed closely with those obtained by the former method, the difficulty of collecting the mercury completely rendered the process untrustworthy.

Determinations have now been made of the ratio $HgCl_2 : Hg$ by the electrolysis of a solution of mercuric chloride. A special method was devised in which the metal was deposited in globular form by means of a mercury cathode, and, without being removed, was washed by decantation, freed from water by means of acetone, and afterwards weighed. The results of five preliminary experiments and of six final experiments each gave a mean value for the atomic weight of mercury, 200·63 (Cl = 35·46), whilst the value obtained in the earlier paper (*loc. cit.*) from the ratio $HgCl_2 : 2AgCl$ was 200·62. E. G.

Ultra-microscopic Observations of the Hydrolysis of Mercuric Chloride. HERMANN W. FISCHER and E. BRIEGER (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 196—197).—An aqueous solution of mercuric chloride has been found to contain a number of ultra-microscopic particles. These are attributed to the formation of a colloidal substance as a result of hydrolytic decomposition. The colloidal product ages with time, and becomes less soluble; this leads to further hydrolytic decomposition and to an increase in the number of ultra-microscopic particles. Rise of temperature has the same effect, and this observation supports the view that the presence of submicrons is due to hydrolysis. The protective influence of sodium chloride on a solution of mercuric chloride is attributed to the diminution of the hydrolysis in consequence of the formation of the complex salt Na_2HgCl_4. H. M. D.

Lutetium and Neoytterbium or Cassiopeium and Aldebaranium. GEORGES URBAIN (*Zeitsch. anorg. Chem.*, 1910, **68**, 236—242).—Claim for priority against Welsbach (Abstr., 1908 ii, 591; compare Abstr., 1908, ii, 283, 849). C. H. D.

The Preparation of Manganic Fluorides and the Titration of Manganese by Volhard's Method in Presence of Fluorides. ERICH MÜLLER and PAUL KOPPE (*Zeitsch. anorg. Chem.*, 1910, **68**, 160—164).—Manganic fluoride has been prepared previously from

mangano-manganic oxide and hydrofluoric acid. A fluoride of tervalent manganese is readily obtained by the action of permanganates on a manganous salt in presence of hydrofluoric acid, the reaction being: $MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} = 5Mn^{\cdot\cdot\cdot} + 4H_2O$. The difference between the reactions in presence of hydrofluoric and sulphuric acids is due to the conversion of $Mn^{\cdot\cdot\cdot}$ into a complex fluoride ion in the former case.

By mixing, in the order given, a solution of 8·9 grams of manganous sulphate in 30 c.c. of water, 8 c.c. of 40% hydrofluoric acid, a solution of 1·58 grams of potassium permanganate in 25 c.c. of water, and one of 5·8 grams of potassium fluoride in 20 c.c., in a platinum basin, a salt is obtained which, after washing with hydrofluoric acid and alcohol and drying in a desiccator, has the composition $2KF,MnF_3,H_2O$.

Manganese dioxide, which is insoluble in hydrofluoric acid, dissolves if a manganous salt is also present. Manganic fluoride, free from potassium, may be obtained by electrolysing a neutral solution of a manganous salt and dissolving the oxide precipitated at the anode in hydrofluoric acid.

The difficulty of observing the end-point in presence of the pink manganic salt makes it impossible to obtain accurate results on titrating manganese with permanganate in presence of hydrofluoric acid. The reaction appears, however, to be nearly complete in a warm solution. The presence of fluorides causes a large error in the titration of manganese by Volhard's method, but not in the titration of ferrous salts. C. H. D.

Electrolytic Conversion of Manganates into Permanganates. KURT BRAND and J. E. RAMSBOTTOM (*J. pr. Chem.*, 1910, [ii], 82, 336—396).—The authors have been forestalled by Askenasy and Klonowsky (this vol., ii, 413) in the publication of their results. The manganate melt for the electrolytic production of potassium permanganate is made by heating manganese dioxide, potassium hydroxide, and a little water at a dark red heat, oxygen being supplied by the atmosphere and not by potassium nitrate or chlorate, since the addition of the latter results in the formation of potassium nitrite or chloride, the presence of either of which during the electrolysis is disadvantageous.

The apparatus consists of a slender glass vessel containing an earthenware vessel in which are the anode of nickel gauze and the anodic liquor, consisting of a solution containing 4% of potassium manganate and 14% of potassium hydroxide; the cathode is also made of nickel, and the surrounding solution is 2·2% potassium hydroxide. The results of the experiments show that the yield of potassium permanganate is appreciably increased by stirring thoroughly the anodic solution, and decreases with increase of the current density at the anode, the highest practicable value being 0·0125 ampere per sq. cm. with a nickel anode, and 0·005 with an iron anode.

The solubility of potassium permanganate in aqueous potassium hydroxide of varying strength has been determined, and it is shown

that the potassium permanganate remaining dissolved in the anodic liquor can be isolated, either by evaporating the solution carefully, protected from dust particles, etc., or by continually adding the solid manganate melt to the anodic solution during the electrolysis, whereby the concentration of the potassium hydroxide becomes ultimately so great that the potassium permanganate is almost entirely precipitated.

C. S.

The System Iron–Nickel. RUDOLF RUER and EMIL SCHÜZ (*Metallurgie*, 1910, 7, 415—420).—The freezing-point curve of the system iron–nickel, determined from quantities of 150 grams, is continuous, with a shallow minimum, and the liquidus and solidus curves practically coincide throughout. Determinations of the temperatures of magnetic transformation yield results in general agreement with those of Guillaume and Osmond, but the boundary between the reversible and irreversible alloys is now placed at 29% of nickel. The maximum of the reversible transformation curve at 618° and the minimum of the freezing-point curve at 1435° both lie near to 70% of nickel, pointing to the existence of a compound $FeNi_2$.

The electrical conductivity of rods cast in narrow magnesia cylinders and annealed by heating to 900° and cooling slowly, shows a minimum at 35% Ni, and the compound $FeNi_2$ is not indicated on the curve.

C. H. D.

Goldschmidt's Ferroboron and Manganese-Boron, and the Residue Obtained on Heating Ferroboron in Hydrogen Sulphide. JOSEF HOFFMANN (*Chem. Zeit.*, 1910, 34, 1045—1046. Compare this vol., ii, 508).—Goldschmidt's borides behave towards reagents as heterogeneous substances, and this view is confirmed by microscopical examination, which shows distinct crystallites in a homogeneous ground mass. Detailed descriptions of some of the crystals are given.

The residue obtained when hydrogen sulphide acts on ferroboron contains borides which are resistant to acids, and also boron sulphide and a sulphur compound which is not ferrous sulphide, but probably a ferrous thioboride.

C. H. D.

Complex Compounds of Cobalt with Chloric and Perchloric Acids. ROBERTO SALVADORI (*Gazzetta*, 1910, 40, ii, 9—18). —A number of cobaltiammine chlorates and perchlorates have been examined. They are all explosive, the chlorates by percussion or on ignition, the perchlorates by percussion or detonation. The perchlorates are very stable at the ordinary temperature, whilst the chlorates decompose slowly, the luteo-derivatives being more stable than the roseo- or purpureo-compounds.

For the analysis, the chlorates are reduced by means of ferrous sulphate in ammoniacal solution, and the perchlorates by fusion with sodium carbonate in a platinum crucible placed in an outer crucible also containing sodium carbonate. Ammonia is estimated by distillation with sodium hydroxide, and cobalt by electrolytic reduction in presence of ammonium oxalate. The metallic deposit contains carbon,

and it is necessary to dissolve it in sulphuric acid, to filter, and to redeposit the cobalt electrolytically.

Luteo-cobaltiammine chlorate, $Co(NH_3)_6(ClO_3)_3,H_2O$, prepared by passing oxygen through a 5% solution of cobalt chlorate in an excess of ammonia at 50°, adding chloric acid, and evaporating, forms yellow crystals, and explodes at 120° if rapidly heated. It may be obtained in an anhydrous form from luteo-cobaltiammine chloride and silver chlorate by cooling the filtrate in a freezing mixture. It then forms yellow needles, soluble in water to the extent of 7·87% at 18°, much more at higher temperatures.

Cobalthydrazine perchlorate, $Co(N_2H_4)_2(ClO_3)_2$, obtained by adding hydrazine hydrate to luteo-cobaltiammine chloride, forms yellow crystals, which are highly explosive. If carbon dioxide is passed into the solution containing hydrazine hydrate, cobalthydrazine carbonate and hydrazine hydrochloride are formed, and nitrogen is evolved, the reaction probably proceeding as follows:

$$Co(N_2H_4)_2(ClO_3)_2 + N_2H_6CO_3 = Co(N_2H_4)_3CO_3 + 2HCl + 6O;$$
$$2HCl + 6O + 5N_2H_4 = 6H_2O + 3N_2 + 2N_2H_5Cl.$$

Roseo-cobaltiammine chlorate, obtained from the mother liquor of the luteo-salt, or from silver chlorate and roseo-cobaltiammine chloride, is a pink, very soluble powder, the solubility in water at 18° being 105·8%. The *purpureo*-salt, also obtained by double decomposition, forms large, garnet-red tetrahedra.

Cobalt perchlorate, $Co(ClO_4)_2,6H_2O$, prepared from cobalt carbonate and perchloric acid, and crystallised slowly, forms prisms 4 cm. long, loses water at 100° to form a violet, hygroscopic powder, and explodes by percussion. When rapidly heated, it deflagrates without exploding. When ammonia and ammonium perchlorate are added to its solution, a red powder having the composition $Co(ClO_4)_2,6NH_3$ is precipitated, ammonia directly replacing water. Boiling water decomposes it according to the equation:

$$2Co(ClO_4)_2,6NH_3 + 2H_2O = Co(OH)_2 + Co(ClO_4)_2 + NH_4ClO_4 + 4NH_3.$$

Other metallic perchlorates behave in a similar manner.

Luteo-cobaltiammine perchlorate, $Co(NH_3)_6(ClO_4)_3,H_2O$, is soluble in water to the extent of 0·967% at 18° (compare Alvisi, Abstr., 1902, ii, 24). *Roseo-cobaltiammine perchlorate*,

$$Co(NH_3)_5,H_2O,(ClO_4)_3,H_2O,$$

and the *purpureo*-salt dissolve in water at 18° to the extent of 7·4% and 11% respectively. C. H. D.

Compounds of Chromium. VIII. Triamminechromium Salts. ALFRED WERNER (*Ber.*, 1910, **43**, 2286—2295).—The starting point in the preparation of triamminechromium salts is triamminechromium tetroxide, for which a new method of preparation is given. To a strongly cooled solution of 30 grams of chromic acid in 300 c.c. of water are added 300 c.c. of pyridine. After remaining for half an hour in a freezing mixture, 750 c.c. of 3% hydrogen peroxide are added. The precipitated pyridine perchromate is collected, washed, and added to 90 c.c. of well-cooled 25% ammonia. The precipitated triamminechromium tetroxide is collected after ten minutes and washed with water, alcohol, and ether.

Trichlorotriamminechromium, $(NH_3)_3CrCl_3$, results when triamminechromium tetroxide is added to cold concentrated hydrochloric acid. A grey to bluish-grey precipitate is formed, and the filtrate from this deposits the trichlorotriamminechromium on keeping for two days. The crystals are dark blue with a greenish tinge. It is almost insoluble in water, in which properties it resembles trichlorotriamminecobalt. It dissolves in hot water, giving a blue solution, from which the dichloroaquotriamminechromium salts (Abstr., 1906, ii, 760) are precipitated by appropriate reagents. The grey to bluish-grey precipitate mentioned above is probably a mixture of dichloroaquotriamminechromium chloride and trichlorotriamminechromium.

Triaquotriamminechromium chloride, YCl_3, where $Y = \left[Cr\begin{matrix}(NH_3)_3\\(OH_2)_3\end{matrix}\right]$, is obtained as follows: A mixture of 1 gram of dichloroaquotriamminechromium chloride with 8 c.c. of water is covered with 5 c.c. of pyridine. The resulting solution is filtered, and the hydroxoiodide precipitated by the addition of solid potassium iodide. The chloride is then obtained by triturating the hydroxoiodide with concentrated hydrochloric acid. After purification by solution in water and precipitation with hydrogen chloride, it forms brownish-red, hygroscopic crystals. It was also prepared by dissolving triamminechromium tetroxide in dilute hydrochloric acid (1 : 4) and saturating the cooled solution with hydrogen chloride. The *chloride-nitrate*, YCl_2NO_3, is precipitated when concentrated nitric acid is added to a cold concentrated solution of the chloride. When nitric acid is replaced by perchloric acid, pale red plates of the *perchlorate*, $Y(ClO_4)_3$, are obtained.

Dibromoaquotriamminechromi-salts, YX, where $Y = \left[Br_2Cr\begin{matrix}OH_2\\(NH_3)_3\end{matrix}\right]$. To prepare the *bromide*, YBr, triamminechromium tetroxide is dissolved in cooled hydrobromic acid (D 1·49), whereby bromine is evolved, and concentrated sulphuric acid added to the well-cooled solution. Intense green crystals are obtained, soluble in water to a green solution, which rapidly turns bluish-red. The *iodide*, YI, *thiocyanate*, YSCN, *nitrate*, YNO_3, and *sulphate*, Y_2SO_4, all form green crystals, and are prepared from a fresh solution of the bromide by precipitation with potassium iodide, potassium thiocyanate, nitric and sulphuric acids respectively. The green colour of these salts corresponds with that of the dichloro- and dibromo-diethylenediaminechromium salts. The dichloroaquotriamminechromium salts are, however, blue. This difference in colour is not due to a difference in constitution, since when the green dibromo-bromide is converted into triaquotriamminechromium nitrate, $\left[Cr\begin{matrix}(OH_2)_3\\(NH_3)_3\end{matrix}\right](NO_3)_3$, by means of silver nitrate, and the dichloroaquotriamminechromium nitrate prepared from this by means of hydrogen chloride, the usual blue salt is obtained. Both the green and the blue salts are therefore praseo-salts.

Bromodiaquotriamminechromi-salts, YX_2, where $Y = \left[BrCr\begin{matrix}(OH_2)_2\\(NH_3)_3\end{matrix}\right]$. Five grams of triamminechromium tetroxide are dissolved in 50 grams

of well-cooled hydrobromic acid (D 1·49). The solution is then boiled until bromine ceases to be evolved, cooled, and 30 c.c. of concentrated sulphuric acid added, whereby a brownish-red, crystalline deposit forms. If this is dissolved in water, the solution rapidly filtered, and the filtrate treated with concentrated hydrobromic acid, reddish-violet crystals of the *bromide*, YBr_2, are obtained. With concentrated hydrochloric acid, the solution of the bromide gives reddish-violet crystals of the *chloride*, YCl_2, from which salt the *sulphate*, YSO_4, may be obtained as violet crystals. The transformation of the chloride into the sulphate proves that the bromine is in the complex.

Hitherto, it has not been possible to isolate the tribromotriammine-chromium, only the following three hydrates of the bromo-series being known, namely: $\left[Br_2Cr{OH_2 \atop (NH_3)_3}\right]Br$, $\left[BrCr{(OH_2)_2 \atop (NH_3)_3}\right]Br_2$, and $\left[Cr{(OH_2)_3 \atop (NH_3)_3}\right]Br_3$. T. S. P.

The Behaviour of Iron towards Solutions of Stannous Salts. ALFRED THIEL and K. KELLER (*Zeitsch. anorg. Chem.*, 1910, **68**, 220—235).—The fact that when iron is added to a solution of the chlorides of tin and antimony, only antimony is precipitated, is in contradiction to the positions of iron and tin in the electrochemical series. It is now shown that tin is actually precipitated, but only in very minute quantity, forming a very thin protecting layer of a tin-iron alloy on the surface of the iron.

Iron dissolves much less rapidly in an acid if a tin salt is present. Measurements of electrolytic potential show that in pure acid tin is always less noble than iron, the difference being greater in stronger acids. In acid containing a stannous salt the potential of iron varies, and finally assumes a value equal, or near, to that of tin, according to the conditions. The deposition of tin on iron is recognisable by analysis, if iron having a relatively large surface, such as turnings, is taken for the experiment.

If iron is introduced into a vessel containing a concentrated electrolyte, containing tin in the lower part, and a more dilute electrolyte free from tin in the upper part, the iron becomes covered with crystals of tin where it dips into the concentrated electrolyte, but remains free from tin if immersed completely in either the concentrated or the dilute solution. C. H. D.

Atomic Weight of Tantalum. CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1910, **32**, 1127—1133).—Owing to the uncertainty existing with regard to the value of the atomic weight of tantalum, determinations have been made of the ratio $2TaCl_5:Ta_2O_5$, the chloride being converted into the oxide by methods similar to those used in the determination of the atomic weight of columbium by Balke and Smith (Abstr., 1908, ii, 1043).

Tantalum chloride was prepared by heating the oxide in a current of chlorine and vapour of sulphur chloride. The chloride was converted into the oxide in quartz bulbs. The bulbs containing the chloride

were placed in a vacuum desiccator with water, and the air was pumped out. The chloride gradually underwent hydrolysis; small quantities of water and concentrated nitric acid were then introduced into the bulb, and the mass was evaporated to dryness. The addition of water and nitric acid and the subsequent evaporation were twice repeated, and the dry mass was finally ignited until no further loss of weight occurred. The mean of eight experiments with three samples of the chloride gave a value for the atomic weight 181·52 (Cl = 35·46), whilst the value given in the international table of atomic weights is 181·0.

Tantalum chloride has D 3·68 at 27°. Specimens of the oxide prepared from the chloride had D varying from 7·91 to 8·62.

E. G.

Easy Method for Preparing Colloidal Gold. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 664—665).—A dilute solution of gold chloride containing a little starch is heated for a short time and then filtered. The filtrate is at first colourless, but gradually becomes deep violet in colour. The starch remaining on the filter paper is coloured violet, and after a few days presents a metallic reflecting surface. On exposing the violet filtrate to diffused light for some days, the gold is slowly deposited.

If the original solution of gold chloride and starch is gently heated for some minutes, the filtrate, which is opalescent, will reduce Fehling's solution. T. S. P.

Mineralogical Chemistry.

A Method for Isolating Native Iron from Basalt without Destroying its Form. MAX SEEBACH (*Centr. Min.*, 1910, 641—643).—Native iron occurs in the basalt of Bühl, near Weimar, in the form of a fine network. The basalt may be removed without destroying the form of the iron by heating with Plattner's flux (10 parts sodium carbonate, 13 parts potassium carbonate, 5 parts borax glass, and 5 parts dry starch) in a graphite crucible. In order to prevent the formation of a thin layer of oxide on the iron, charcoal may be mixed with the flux, and the whole covered with a layer of sodium chloride. A piece of basalt 1 c.c. in size is destroyed in one and a-half hours. The last traces of rock enclosed in the meshes of the iron are removed by fusion with boron trioxide. When it is only required to isolate the iron, without preserving its form, it is best to crush the basalt and fuse with boron trioxide. C. H. D.

Diffusion of Crude Petroleum through Fuller's Earth. J. ELLIOTT GILPIN and OSCAR E. BRANSKY (*Amer. Chem. J.*, 1910, **44**, 251—303).—Gilpin and Cram (Abstr., 1909, i, 1) have shown that when petroleum is allowed to diffuse upwards through tubes packed

with fuller's earth, fractionation takes place, and the fractions rising to the top of the tubes are of lower sp. gr. than those at the bottom. The paraffin hydrocarbons collect in the upper parts of the tubes, and the unsaturated hydrocarbons in the lower parts.

A study has now been made of the behaviour of crude Illinois petroleum when treated in this way. Gilpin and Cram's results have been confirmed, and it has been found that the amount of the sulphur compounds, like that of the unsaturated hydrocarbons, increases gradually from the lightest oil at the top to the heavier oils at the bottom of the tube. When a solution of benzene in petroleum is allowed to diffuse through fuller's earth, the benzene, like the olefines and sulphur compounds, tends to accumulate in the lower part of the tube.

When fuller's earth, which has been used for such diffusion experiments and afterwards treated with water in order to remove as much oil as possible, is dried and extracted with ether, oils of high specific gravity and viscosity are obtained containing considerable quantities of unsaturated hydrocarbons and sulphur compounds. It is therefore evident that fuller's earth exercises a selective action on the petroleum.

A discussion is given of the causes of the differences between the various oils of the United States. Pennsylvania petroleum differs from those of Ohio, Texas, and California in containing a much larger proportion of paraffin hydrocarbons and a much smaller proportion of benzene, unsaturated hydrocarbons, and compounds of sulphur and of nitrogen. In view of the results of the present investigation, it is suggested that this difference may be explained by assuming that the Pennsylvania petroleum has diffused upwards through porous media, such as shales, limestones, and sandstones, and thus undergone fractionation, resulting in the removal of the unsaturated and aromatic hydrocarbons and the sulphur compounds. It is probable that the nitrogen compounds also behave like the unsaturated hydrocarbons and sulphur compounds, and this question is being studied. E. G.

Grahamite, a Solid Native Bitumen. CLIFFORD RICHARDSON (*J. Amer. Chem. Soc.*, 1910, **32**, 1032—1049).—There is a regular gradation in properties and composition between paraffins, asphalts, manjaks, and grahamites, corresponding probably with different stages of metamorphosis. The author discusses the relations between these minerals, and suggests that the term "grahamite" should be confined to that type of solid, native bitumen characterised by a schistose or hackly fracture, by its sparing solubility in naphtha, and by a high percentage of residual coke.

A list of occurrences of grahamite in America is given in tabular form, with the physical properties, percentage of bitumen, and ultimate composition of the bitumen. The bitumen from a typical grahamite from West Virginia gave C 86·56, H 8·68, and S 1·79%. The ash of grahamites contains vanadium, that of a specimen from the Impson Valley containing 11—15% of V_2O_3 (compare Hewett, this vol., ii, 719). Trinidad bitumen should be classed as a grahamite rather than as a manjak. W. O. W.

Mosesite, a New Mercury Mineral from Terlingua, Texas. FREDERICK A. CANFIELD, WILLIAM F. HILLEBRAND, and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 202—208).—The mineral occurs as minute simple octahedra, or spinel-twins, on calcite, and is canary-yellow with an adamantine lustre. It is a mercury-ammonium compound with chlorine (about 5%) and sulphate (about 3·5% SO_4), being thus similar to kleinite (Abstr., 1907, ii, 788), but probably with mercurous, rather than mercuric, sulphate and chloride. In hydrochloric acid it is very slowly changed to calomel, whilst kleinite is completely, although very slowly, dissolved. Heated gradually in a bulb-tube, mosesite first changes colour to black, then to white, and at a higher temperature volatilises, giving sublimates of calomel and mercury. The crystals are optically birefringent, but they become isotropic at 186°; on cooling they revert very slowly to the birefringent modification. Kleinite shows the same change from the optically birefringent to the isotropic state at a slightly higher temperature.

L. J. S.

The Synthetic Sapphires of Verneuil. ALFRED J. MOSES (*Amer. J. Sci.*, 1910, [iv], 30, 271—274).—The crystallised corundum of a fine sapphire-blue colour prepared artificially by A. Verneuil (this vol., ii, 212) gave, on analyses by M. A. Lamme, Al_2O_3, 99·83—99·85%; TiO_2, 0·11—0·13%; Fe_2O_3, trace; SiO_2, nil; D 3·977—4·01. Refractive indices (sodium-light), $\omega = 1·7680$, $\epsilon = 1·7594$. The pleochoism is distinct (ω, indigo-blue, ϵ, pale blue). The optical interference-figure varies from uniaxial to slightly biaxial in character, and the optic axis is inclined at about 40° to the axis of the conical mass.

L. J. S.

Lanthanite. GUSTAF LINDSTRÖM (*Jahrb. Min.*, 1910, ii, Ref. 15; from *Geol. För. Förh. Stockholm*, 1910, 32, 206—214).—Lanthanite of D 2·69—2·74, collected from cerite specimens from Bastnäs, Sweden, gave on analysis:

$(La,Di)_2O_3$.	Ce_2O_3.	Y_2O_3.	CO_2.	H_2O.	Insoluble.	Total.
28·34	25·52	0·79	21·95	23·40	0·13	100·13

This, like the analyses of American lanthanite, agrees with the formula $R_2O_3,3CO_2,8H_2O$.

Hisinger's analysis of "hydrofluocerite" from Bastnäs has come to be wrongly quoted in the text-books under lanthanite, owing to the incorrect translation of the Swedish "flusspatssyra" as "carbonic acid" in an early abstract in *Edin. J. Sci.*, 1826.

L. J. S.

New Occurrence of Hydrogiobertite. ROGER C. WELLS (*Amer. J. Sci.*, 1910, [iv], 30, 189—190).—The material occurs in considerable amount as a white encrustation on shale in Chiles Valley, Napa Co., California, and has been deposited from the water of springs; the serpentine-rocks occurring in the neighbourhood probably supplied the magnesium. The structure is spherulitic, and the spherules often contain a nucleus of shale; D 2·152. Analyses of material containing

admixed shale gave the following results, agreeing with the hydrogiobertite formula: $2MgO,CO_2,3H_2O$.

Insoluble.	$(Al,Fe)_2O_3$.	CaO.	MgO.	CO_2.	H_2O.	Total.
25·33	1·90	2·60	31·81	18·06	20·06	99·76
14·93	1·06	1·84	36·40	23·71	20·81	98·75

L. J. S.

Analyses of Minerals from Croatia. FR. TUĆAN (*Jahrb. Min.*, 1910, ii, Ref. 39—41; from *Glasnik* [*Berichte*] *kroat. naturw. Ges.*, *Agram*, 1907, **19**).—I. Dolomite from the Fruška mountains; pale green, coarsely granular, from serpentine-rocks. II. Magnesite from the Bušnica stream near Trgove; milk-white, compact with conchoidal fracture, from serpentine-rocks. III. Magnesite from the Beočinski potok stream in the Fruška mountains; similar to the last. IV—VI. Strontianocalcite from Radoboj; fibrous aggregates associated with strontianite. VII. Hydrozincite from Ivanec in the Ivančica mountains; milk-white, reniform aggregates associated with smithsonite. VIII—X. Muscovite from the pegmatites at various localities in the Krndija mountains.

	Al_2O_3.	FeO.	MnO.	CaO.	SrO.	MgO.	CO_2.	Insol.	Total.
I.*	0·21	1·53	1·30	30·78	trace	19·47	46·80	0·10	100·19
II.	0·62	1·80	trace	0·37	—	41·98	47·29	8·61	100·67
III.†	0·57	4·39	trace	0·23	—	30·94	36·84	27·01	99·98
IV.	—	trace	trace	54·11	2·26	—	43·51	0·10	99·98
V.	—	trace	trace	40·59	19·32	—	40·05	—	99·96
VI.	—	trace	trace	53·07	3·66	—	43·26	—	99·99
VII.‡	—	1·25	—	0·20	—	—	14·30	—	100·27

* NiO, trace. † Na_2O,K_2O,Li_2O, trace. ‡ ZnO, 73·75; H_2O, 10·77.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	H_2O.	Total.
VIII.	47·72	28·70	7·24	0·58	trace	0·54	—	7·31	1·92	trace	6·34	100·35
IX.	46·93	34·32	3·18	—	trace	0·63	0·21	5·89	2·42	trace	5·83	99·41
X.	46·66	37·40	2·32	0·18	trace	0·53	trace	6 09	2·41	trace	4·98	100·57

L. J. S.

Chalybite from Croatia. FR. TUĆAN (*Jahrb. Min.*, 1910, ii, Ref. 12; from *Nastavni vjesnik*, *Monatsber. kroat. Mittelschulver.*, *Agram*, 1908, **17**).—Fourteen analyses are given of chalybite from various localities in Croatia. L. J. S.

New Occurrence of Plumbojarosite. WILLIAM F. HILLEBRAND and FRED. E. WRIGHT (*Amer. J. Sci.*, 1910, [iv], **30**, 191—192. Compare Abstr., 1902, ii, 667).—The mineral was found at American Fork, Utah, as friable lumps consisting of minute, brownish-red, glistening crystals with pyromorphite and calcite. The crystals are rhombohedral, with the basal pinacoid largely developed, and a rhombohedron ($cr = 53°40'$ about); they are optically uniaxial and negative, and strongly dichroic. Analysis gave:

Fe_2O_3.	PbO.	K_2O.	Na_2O.	SO_3.	H_2O.	CuO.	CaO.	Insol.	Total.
42·87*	18·46	0·15	0·52	27·67	10·14	0·10	0·06	0·40	100·37

* Including very little P_2O_5 and probably some Al_2O_3.

L. J. S.

Oxalite from Cape d'Arco (Island of Elba). ERNESTO MANASSE (*Atti. R. Accad. Lincei*, 1910, [v], **19**, ii, 138—145).—The mineral was found in a vein of oxide and hydroxide of iron and manganese, which also contains pyrites and galena. It forms small, transparent prisms or tablets of an amber-yellow colour, hardness about 2, D 2·28. Analysis leads to the formula $FeC_2O_4,2H_2O$

FeO.	MgO.	C_2O_4.	H_2O (by difference).
40·72	trace	40·18	19·10

An oxalate of similar composition, but only microcrystalline, was prepared from ferrous ammonium sulphate or ferrous chloride, with oxalic acid. The crystallographic examination of the mineral gave [$a:b:c=0·77297:1:1·10392$]. The crystals are birefractive to an unusual degree. R. V. S.

Mizzonite from Cape d'Arco (Island of Elba). ERNESTO MANASSE (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 211—215).—The mineral was found in association with quartz in small veins of manganese oxide and hydroxide in a mine which yields iron and manganese. In close proximity occur crystalline schists and calcite of presilurian origin. It has hardness 5—6, and D 2·60. The crystals are prismatic, have a nacreous lustre, and are birefractive. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Cl.	Loss at red heat	Total.
54·40	24·44	trace	10·19	trace	7·59	1·69	1·53	1·43	101·27

which is in agreement with those required by the amorphous mixture,

$$\{Na_4[AlCl]Al_2[Si_3O_8]_3\}_3\{Ca_4[AlO]Al_2[Si_2AlO_8]_3\}_2.$$

The values observed for the indices of refraction and the birefraction are also in accord with this structure. R. V. S.

Minerals from Ruwenzori. LUIGI COLOMBA (*Jahrb. Min.*, 1910, ii, Ref. 41—42; from "*Il Ruwenzori*" *by the Duca degli Abruzzi, Milano*, 1909, **2**, 281—286).—The minerals collected from the amphibolite, granite, and pegmatite are described, and analysis given of the following: I—IV, Epidote, as small, striated needles (I, greyish-green; II, pale green; III, brownish-green; IV, colourless, from Lake of Garda in northern Italy). In analysis III the ratio of

$$SiO_2:R_2O_3:(RO,R_2O)=10:5:9,$$

whilst in the others it is 2 : 1 : 2. V, Albite, as small crystal druses in crevices; VI, Microcline, massive; VII, Garnet (pyrope), as bright red, distorted crystals associated with microcline; VIII, Ilmenite, indistinct crystals, associated with albite:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	38·21	30·84	—	7 25	20·43	0·38	—	—	2·71	99·82
II.	37·63	31·41	—	4·38	23·70	—	—	—	2·19	99·31
III.	38·31	23·47	12·29	—	23·52	—	—	—	2·42	100·01
IV.	37·95	30·38	—	7·83	20·34	0·93	—	—	2·64	100·07
V.	67·43	20·15	—	—	1·43	—	—	10·27*	—	99·28
VI.	64·30	19·69	—	—	—	—	15·33	0·71	0·40	100·43
VII.†	41·43	24·71	1·37	10·31	5·33	16·51	—	—	—	99·66

* With a little K_2O. † MnO, trace.

	TiO_2.	FeO.	Fe_2O_3.	MgO.	Total.
VIII.	52·73	45 83	nil.	1·25	99·81

L. J. S.

A Garnet containing Iron and Chromium from Praborna (St. Marcel). LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 146—150).—The mineral occurs in association with hæmatite, quartz, albite, and titanite, whilst native gold and kammererite are also to be found in the same situation. Analysis yielded the following figures:

SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	CaO.	MgO.	MnO.	FeO.	Total.
35·57	0·62	22·22	7·81	27·13	trace	3·94	2·51	99·80

which correspond, when the small amount of aluminium is neglected, with the typical garnet composition $R_3''(R_2')^{VI}Si_3O_4$. From a comparison of the analytical data with those found for various specimens of uvarowite, the author considers it probable that this mineral also belongs to that group. It has D 3·81, and is very strongly birefractive.

R. V. S.

Gageite, a New Mineral from Franklin, New Jersey. ALEXANDER H. PHILLIPS (*Amer. J. Sci.*, 1910, [iv], **30**, 283—284).—This is found in very small amount as delicate acicular and hair-like, colourless crystals arranged in radiating bundles, and is associated with zincite, willemite, calcite, and leucophœnicite. When heated, the clear crystals lose water and assume a deep bronze colour. Analysis by R. B. Gage gave:

SiO_2.	MnO.	ZnO.	MgO.	H_2O.	Total.
24·71.	50·19	8·76	11·91	[4·43]	100·00.

Formula: $8RO,3SiO_2,2H_2O$. The mineral appears to be closely related to leucophœnicite (Penfield and Warren, Abstr., 1900, ii, 89), and it is, perhaps, one of the undescribed species mentioned by Penfield and Warren.

L. J. S.

The Chemical Composition of the Stassfurt Salt Clays. E. MARCUS and WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1910, **68**, 91—101).—The portion soluble in water is estimated by boiling with water and washing until no more chlorine passes through. The main analysis is made by Hillebrand's method. Water is estimated by heating with dried sodium carbonate or lead oxide in a current of air. The methods employed are described in detail. In the following analyses, arranged in order of depth, I is a hard salt clay, II a shaly salt clay, III a soft loamy clay, and IV a hard clay immediately in contact with the anhydrite.

Soluble in Water:

	NaCl.	KCl.	$MgCl_2$.	K_2SO_4.	$CaSO_4$.	$MgSO_4$.
I.	0·36	—	—	16·94	36·11	12·06
II.	0·61	0·31	0·73	—	35·14	0·94
III.	1·09	0·40	5·41	0·33	1·19	—
IV.	0·23	0·16	1·44	—	0·92	0·74

Insoluble:

	$CaSO_4$.	CaO.	$MgCO_3$.	MgO.	K_2O.	Na_2O.	Al_2O_3.	Fe_2O_3.	FeO.	Mn_3O_4	ZnO.	SiO_2.
I.	22·72	0·53	—	1·56	0·11	0·26	0·78	0·40	0·05	—	trace	2·98
II.	27·06	0·88	—	3·88	0·61	0·005	4·51	0·50	0·49	0·14		19·46
III.	0·87	—	—	10·41	2·53	0·38	17·04	2·00	1·56	0·27	0·11	37·80
IV.	0·70	—	75·43	0·54	0·29	0·09	2·16	0·37	1·51	0·10		11·17

	TiO_2.	P_2O_5.	H_2O.	C.	CO_2.	S.	Vd_2O_3.	Total (corrected).	Bitumen.
I.	0·05	trace	4·51	0·07	0·69	trace	—	100·22	0·11
II.	0·24	0·01	3·99	0·15	0·53	trace	<0·02	100 21	0·15
III	0·64	0·13	16·39	0·16	0·75	0·03	0·02	99·52	0·12
IV.	0·13	0·08	3 94	0·22	—	0·03	<0·01	100·25	0·11

All contain traces of lithium and chromium, and all but (I) also contain small quantities of boric acid and bromine. The minute quantities of ammonia, nitrates, and copper have been recorded previously (Abstr., 1909, ii, 571, 1011). C. H. D.

The Amount of Thorium in Sedimentary Rocks. II. Arenaceous and Argillaceous Rocks. JOHN JOLY (*Phil. Mag.*, 1910, [vi], 20, 353—357).—Whereas the calcareous rocks show a small, almost negligible, quantity of thorium (compare this vol, ii, 723), the detrital sediments in almost every case contain easily measured amounts, the argillaceous group having almost double the amount in the arenaceous group. For the former 1·3, and for the latter 0·6 ($\times 10^{-5}$ gram per gram), may be taken as average values. Twelve specimens of arenaceous and conglomeritic rocks, mainly sandstones, were examined, and eighteen specimens of argillites, mainly slates. A specimen designated as "Grauwacke, Wipperfürth, Rhen-Prussia, Middle Devonian" gave the highest result (2·4). The higher thorium content of the slates and shales is attributed to the sorting out by gravity of the large particles of quartz or felspar which are poor in radioactive constituents. F. S.

Physiological Chemistry.

Influence of a Rise of Body Temperature on the Blood Gases. WILHELM CASPARI and ADOLF LOEWY (*Biochem. Zeitsch.*, 1910, **27**, 405—417).—At great altitudes (Monte Rosa) a rise of body temperature is very frequent, and symptoms of acidosis occur. The fall in the oxygen tension is compensated for by increased respiration, so that the oxygen in the tissues is but little affected; the elevation of body temperature and the acidosis are favourable factors for the dissociation of oxyhæmoglobin in the tissues. The body is thus able to compensate for the alterations in pressure. The heart is not affected.

W. D. H.

The Gases of Cat's Blood. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1910, **41**, 60—63).—Data of the gases in cat's blood are scanty; the authors used their new form of gas pump. The following are the mean figures of numerous analyses. In the third line the analyses were made with a Töpler-Barcroft pump; here the nitrogen values were between 1·5 and 4%; these have been adjusted to 1·00 to make the figures comparable to those in the first

line. The cats used were killed either by a blow on the head or were anæsthetised with urethane:

	Total gas.	CO_2.	Oxygen.	Nitrogen.
Arterial blood	39·68	25·07	13·60	1·00
Venous blood	51·53	40·83	9·93	0·77
Arterial blood............	33·29	17·69	14·61	1·00

W. D. H.

Cryoscopy of Blood. W. R. G. ATKINS (*Bio.-Chem. J.*, 1910, **5**, 215—216).—A few observations on the value of Δ for the blood of various animals; some amount of variation is noted, and in some cases this may have been pathological. W. D. H.

The Inorganic Constituents of the Blood in Vertebrates and Invertebrates and Its Origin. ARCHIBALD B. MACALLUM (*Proc. Roy. Soc.*, 1910, *B*, **82**, 602—624. Compare Abstr., 1904, ii, 495).—Analyses of the ash of the blood in various animals are given and compared with the saline contents of the ocean at various geological periods. The arguments advanced are speculative, but the facts so far as at present collected support the author's previous conclusion that the saline composition of the sea determines that of the blood of marine organisms, and that the inorganic composition of vertebrate blood-plasma is an heirloom of life in the primeval ocean. The date of the origin of the vertebrate kidney is placed between the second eighth and the second sixth of the whole geological period.
W. D. H.

Hæmolysis. Is there a Cocaine Hæmolysis? GEORG FISCHER (*Pflüger's Archiv*, 1910, **134**, 45—58).—Cocaine solutions have no specific hæmolytic power, but such hæmolysis as occurs is due to dissociation and liberation of hydrogen ions, or to decomposition of the cocaine molecule and liberation of hydrogen ions and alcohol.
W. D. H.

Origin and Destiny of Cholesterol in the Animal Organism. VII. The Quantity of Cholesterol and Cholesterol Esters in the Blood of Rabbits Fed on Diets containing Varying Amounts of Cholesterol. MARY T. FRASER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1910, *B*, **82**, 559—568).—When cholesterol is given with the food, some is absorbed, and the free cholesterol and the cholesterol esters in the blood are increased. If phytosterol is given, this substance is partly absorbed, and the free cholesterol of the blood rises. Phytosterol does not appear in the blood as such.

The digitonin method for estimating cholesterol is very accurate.
W. D. H.

Action of Acids and Alkalis on the Artificial Anti-serum of the Ox, which is Hæmolytic to Rabbits. GIOVANNI MORUZZI (*Biochem. Zeitsch.*, 1910, **27**, 498—515).—Hydrochloric acid completely inhibits the hæmolysis when present to the extent of $0·015N$; it does

not destroy the hæmolytic power, for this again becomes evident on neutralisation. There is no destruction either of the amboceptor or the complement. Dilution with normal saline solution does not revive the process. Similar experiments with sodium hydroxide show many analogies to the action of hydrochloric acid. There is no increase in viscosity in either case. W. D. H.

The Relationship between the Anti-trypsin of the Blood and that of the Urine. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, **27**, 397—404).—In artificial nephritis in rabbits there is a great rise in the anti-trypsin of the urine and of the blood. In nephritis produced by uranium salts, the rise is first seen in the urine; in that produced by chromic acid, first in the blood; in spontaneous albuminuria and in that produced by mercuric chloride, the rise in both fluids is simultaneous. W. D. H.

Inhibition of Precipitation by Precipitoids. WILHELM SPÄT (*Biochem. Zeitsch.*, 1910, **28**, 7—15).—The experiments described show that the inhibition of precipitation produced by inactivated immune serum or normal serum is not brought about by a union between the inactive serum (precipitoid) and extracts of bacteria employed. W. D. H.

Estimation of Adrenaline in Normal Blood and after its Injection by means of Physiological Methods. PAUL TRENDELENBURG (*Arch. exp. Path. Pharm.*, 1910, **63**, 161—176).—The physiological test adopted was in principle that of Laewen (*ibid.*, 1904, **51**, 415), namely, the measurement of the vaso-constrictor effect on the frog's hind limbs by the rate of outflow when perfused with the substance dissolved in Ringer's solution. The quantity of adrenaline in the blood stream of cats after an injection runs parallel to its pressor effect. As the blood pressure falls, the amount of adrenaline in the circulation sinks. Adrenaline thus resembles muscarine in its rapid disappearance. W. D. H.

Specific Adaptation of Digestive Juices. I. Specificity of Gastric and Pancreatic Juice. E. S. LONDON and W. N. LUKIN. **II. Specificity of Duodenal Mixed Juices.** E. S. LONDON and R. S. KRYM. **III.** E. S. LONDON and N. DOBROWOLSKAJA (*Zeitsch. physiol. Chem.*, 1910, **68**, 366—370, 371—373, 374—377).—I. From experiments on fistulous dogs, varying kinds of food placed in the intestine lead to specific variations in the quantity of bile and pancreatic juice secreted, but not to variations in the amounts of the pancreatic enzymes. When fat is introduced, there is no increase (five cases out of seven) in the lipase secreted in the "small stomach."

II. The same is true for the mixture of juices in the duodenum when the food is introduced into the lower jejunum and ileum.

III. There is similarly no adaptation of the enzymes of the intestinal juice. Oleic acid and amino-acids are specially powerful stimulants in regard to the amount of juice secreted. W. D. H.

The Laws of Digestion and Absorption. VI. The Distance Law of Solution by Duodenal Juice. E. S. LONDON and C. SCHWARZ. **VII. The Neutralisation Laws of Digestive Juices.** E. S. LONDON and O. J. GOLMBERG. **VIII. The Action of Various External Factors on the Secretion of Duodenal Juices. IX. Digestion of Carbohydrates.** E. S. LONDON and A. P. KORCHOW (*Zeitsch. physiol. Chem.*, 1910, **68**, 346—351, 352—357, 358—362, 363—365. Compare this vol., ii, 422).—VI. By experiments on dogs with fistulæ, it was found that the effect of an acid peptone solution in calling forth the secretion of the pancreas and liver is not limited to the duodenum, but extends as far as the upper ileum, a distance of about 2 metres; this action in stimulating secretion diminishes analwards with the square root of the distance from the point of stimulation.

VII. The quantity of pancreatic juice is directly proportional to the square root of the concentration of the gastric juice, and its alkalinity inversely proportional. The total amount of alkali in the duodenal juices is inversely proportional to the square root of the gastric juice concentration.

VIII. Further laws are laid down in regard to the duodenal juices (bile, pancreatic juice, intestinal juice), in all of which the square root figures largely.

IX. Three hours after a meal of flesh and starch in a dog, the stomach contents contain the same amount of starch, although the amount given varies from 40 to 100 grams. W. D. H.

The Chemistry of Digestion and Absorption in the Animal Body. XL. The Study of Gastric Digestion on a Mixed Protein Diet. E. S. LONDON and C. SCHWARZ (*Zeitsch. physiol. Chem.*, 1910, **68**, 378—380. Compare this vol., ii, 422).—Gastric digestion is specially furthered by those proteins (such as meat compared with egg-white) which stay longest in the stomach. W. D. H.

Digestion of Fat in the Stomach and Small Intestine, and the Effect of Lecithin on it. USUKI (*Arch. exp. Path. Pharm.*, 1910, **63**, 270—293).—If lecithin or egg-yolk is mixed with milk, the rate of fat digestion is increased, and the contents leave the stomach sooner. The addition of lecithin lessens the amount of soaps in the intestine, and increases it (after egg-yolk) in the fæces; this is explained by absorption processes in the large intestine. The splitting of lecithin in the stomach occurs more quickly than that of neutral fats. Lecithin favours the saponification and digestion of neutral fats. In spite of its small percentage of lecithin, fat digestion is more favoured by egg-yolk than by lecithin itself; this is probably due to the fineness of the emulsion as well as the chemical nature of the fat in yolk. No lecithin was found in the intestine; it must therefore be split up either in the stomach or soon after its entrance into the duodenum. The observations were made on dogs and children. W. D. H.

Phosphorus Metabolism in the Animal Organism. FELIX ROGOZIŃSKI (*Bull. Acad. Sci. Cracow*, 1910, *B*, 260—312).—Sodium

phosphate, phytin, and lecithin, added to the diet of a grown dog, produce no marked change in nitrogenous metabolism. Sodium phosphate is excreted quantitatively in the urine. Lecithin when given is not found in the fæces; its phosphoric acid appears quantitatively as inorganic phosphate in the urine; the phosphorus of phytin appears to the extent of 30% as phosphoric acid in the urine; the remainder is found as phytin in the fæces. In opposition to the work of others, phytin in man causes no change in the excretion of nitrogen or phosphorus; a small part of the phosphorus is retained; the remainder appears as inorganic phosphate in the fæces. In contrast with the dog, human fæces contain abundant lecithin compounds. No inositol is found in human urine after feeding on phytin. The bacteria of human fæces are able *in vitro* to decompose phytin and produce inorganic phosphates from it. W. D. H.

Physiological Protoplasmic Metabolism and Purine Formation. F. MAREŠ (*Pflüger's Archiv*, 1910, **134**, 59—102).—The various theories of the origin of purine substances, especially uric acid (for instance, the muscular theory, the leucocyte theory, etc.), are discussed at length. Purely chemical views are discountenanced, for the source of purine is to be sought in the physiological activity of the living cell. The constancy of uric acid excretion in individuals is true only for fasting periods, and considerable stress is laid on the importance of the work of the digestive organs as a means of increasing uric acid formation. The nucleus of the cell is the main part concerned, and the same is true for other active cell masses, for instance, malignant growths. The importance of the digestive glands is shown by the fact that pilocarpin raises the uric acid output. W. D. H.

The Metabolism of Some Purine Compounds in the Rabbit, Dog, Pig, and Man. LAFAYETTE B. MENDEL and JOHN F. LYMAN (*J. Biol. Chem.*, 1910, **8**, 115—144).—The examination of tissue extracts has shown that in different animals the purine enzymes are differently distributed; the present experiments, in which purines were given either parenterally (in animals) or by the mouth (in man) support the view that the metabolic history of the purines varies in different animals. The difficulty man has in oxidising uric acid, as shown by its reappearance in the urine after parenteral administration, fits in with the examination of tissue extracts, in which no uricolytic enzyme is found in human tissues. On the other hand, a large proportion of the uric acid introduced into the rabbit does not reappear as such. After injection of adenine in dogs and rabbits, there is a relatively large output of unaltered adenine, and but little uric acid or allantoin. If guanine is given, there is a larger output of allantoin, xanthine, and uric acid. Guanase is more widespread in rabbit and dog tissues than adenase. In the pig, uric acid is not the chief end-product of purine metabolism. In man, the protocols given emphasise the fact that all the ordinary purines lead to an increase of exogenous uric acid, with but little influence on the elimination of purine bases in the urine.

W. D. H.

Cleavage of Histidine in the Organism of the Dog. EMIL ABDERHALDEN, HANS EINBECK, and JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, **68**, 395—399. Compare Abstr., 1909, ii, 906).—Intravenous administration of histidine in a dog does not lead to increase in the excretion of allantoin in the urine. If given by the mouth, the increase of allantoin is very slight, and sometimes absent. Very little of the histidine given (0·4 out of 20 grams) is recoverable as such in the urine. Nucleic acid raises the allantoin excreted. W. D. H.

Influence of the Removal of Fragments of the Gastro-intestinal Tract on the Character of Nitrogen Metabolism. III. The Excision of the Stomach. A. CARREL, GUSTAVE M. MEYER, and PHŒBUS A. LEVENE (*Amer. J. Physiol.*, 1910, **26**, 369—380. Compare this vol., ii, 323).—Two dogs were operated on, and in one of them the extirpation of the stomach was quite complete. Before the tenth week there is high nitrogen retention, probably because the pancreatic and intestinal secretions are interfered with, but after this date no nitrogen retention occurs. Parenterally introduced protein was completely retained in the organism.
W. D. H.

Imbibition of the Intestinal Mucous Membrane with Sodium Chloride and Sulphate Solutions of Different Concentrations. G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1910, **27**, 516—529).—The present experiments deal with sodium sulphate; they support Loeper's conclusions, and show that the salt has an inhibitory influence on imbibition, but this is regarded as a secondary effect; the opinion is held that it is the ions working on the intestinal muscle which explains the purgative action of the salt. W. D. H.

The Influence of Sugar on the Permeability of the Intestinal Membrane. ERNST MAYERHOFER and ERNST STEIN (*Biochem. Zeitsch.*, 1910, **27**, 376—384).—The permeability of the intestinal mucous membrane of rabbits, removed after death, is increased towards normal ammonium chloride solution by placing the membrane in a 5% solution of dextrose. Supposing the same to be true *in vivo*, cases of dyspepsia due to excess of sugar are explicable. W. D. H.

The Fate of Sucrose after Parenteral Introduction in Animals. LAFAYETTE B. MENDEL and ISRAEL S. KLEINER (*Amer. J. Physiol.*, 1910, **26**, 396—406).—When sucrose is introduced intraperitoneally or subcutaneously into dogs and cats in doses of 1—2 grams per kilo. of body-weight, about 65% is recovered in the urine, and a reducing lævorotatory substance is also sometimes present. The excretion begins within a few minutes, and is usually completed in thirty-six hours. The actual figure, however, varies with different conditions (fasting, pregnancy, etc.). Sucrase was not found in the blood; nevertheless, as Abderhalden and Brahm showed, there is a possibility of sucrose digestion in the blood, which may account for the disappearance of part of the sugar. W. D. H.

The Value of Beer-extract and Beer in the Human and Animal Organism. WILHELM VÖLTZ, RUDOLF FÖRSTER, and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1910, **134**, 133—258).—The dry residue of beer extract elevates the absorption of non-nitrogenous material, especially fat. Approximately 40% of the nitrogenous substance is absorbed. Observations both on men and dogs are given, and deductions as to its nutritive value coincide in the main with those of Atwater and Benedict. Observations with toxic doses are also given. The general trend of the article is a defence of the use of alcohol in moderation, especially in the form of beer. W. D. H.

Digestibility of Bleached Flour. ELBERT W. ROCKWOOD (*J. Biol. Chem.*, 1910, **8**, 327—340).—Experiments on the artificial digestion of unbleached flour, as compared with specimens of the same flour bleached with nitrogen peroxide, show no loss of digestibility, and in some cases the bleached specimens digested more rapidly than the unbleached. W. D. H.

The Value of the Cleavage Products of Protein in the Animal Organism. XVI. EMIL ABDERHALDEN and AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, **68**, 416—420. Compare this vol., ii, 877).—A dog was fed exclusively on the cleavage products of flesh without admixture of fat or carbohydrate. The preparation used was "ereptone," made from meat by the successive action of gastric, pancreatic, and intestinal juices. Vomiting and diarrhœa were to some extent overcome by giving the food carefully in small doses through a gastric fistula. The animal gained in weight, and put on flesh. The conclusions drown by Voit and Zisterer (this vol., ii, 425) from somewhat similar experiments are criticised. W. D. H.

The Temperature-coefficient of Cytolysis in the Unfertilised Egg of the Sea-Urchin. A. R. MOORE (*Quart. J. exper. Physiol.*, 1910, **3**, 257—260).—The temperature-coefficient for the process of cytolysis of sea-urchin eggs in sea-water was found to be about 200 for a difference in temperature of 10°. The same figure was calculated from Gros's data for hæmolysis. W. D. H.

Differentiation of Proteins of Closely Related Species by the Precipitin Reaction. D. A. WELSH and H. G. CHAPMAN (*J. Hygiene*, 1910, **10**, 177—184).—It is possible to distinguish heterologous proteins of closely related species by precipitin interactions arranged with regard to the fact that in the conditions of experiment the weight of precipitates is proportional to the weight of the anti-serum employed. This is illustrated by experiments with the albumin prepared from different birds' eggs. The experiments support the authors' previously expressed view that the anti-serum is the main source of the precipitate in the precipitin reaction. W. D. H.

Chemico-Physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 162—169. Compare this vol., ii, 143).—The authors have

investigated the influence of various chlorides (those of sodium, potassium, calcium, and magnesium) and of various sodium salts (chloride, nitrate, acetate, sulphate, and tartrate) on the imbibition of water by the crystalline lens. Solutions of the following concentrations were employed: *N*/5, *N*/50, *N*/100, *N*/150, *N*/200. In all cases the imbibition was less than that which occurs when the lens is immersed in pure water, and the decrease was greater in the case of the *N*/5-solutions than with the weaker ones. As regards the specific actions of the different ions (for the elucidation of which the results with the strongest solutions are the most trustworthy), it appears that the bivalent cations (magnesium and calcium) diminish the imbibition more than the univalent cations (sodium and potassium), although there are considerable irregularities, which are still more pronounced in the case of the different anions. R. V. S.

Heart Metabolism. I. Metabolic Investigations of the Surviving Warm-blooded Heart. Erwin Rohde (*Zeitsch. physiol. Chem.*, 1910, **68**, 181—235).—Previous work on the isolated mammalian heart, such as that by Locke and Rosenheim on its capacity to utilise sugar, or of Barcroft and Dixon on its gaseous metabolism, is on the whole confirmed; the special feature of the apparatus here used is that simultaneously means are adopted for measuring the work of the heart. The metabolic changes run parallel to the amount of work done. In the presence of sugar, not only is sugar burnt, but often constituents in the heart itself (reserve material) are burnt also, and thus leads to the production of carbon dioxide. When sugar or other nutritive material is absent, these reserve materials are alone utilisable; these probably originate from fat and protein, and the hypothesis is put forward that the heart forms a sort of internal secretion in which glycolysis occurs. W. D. H.

The Injury to the Heart's Activity Produced by Glyoxylic Acid. R. H. Kahn and Emil Starkenstein (*Pflüger's Archiv*, 1910, **133**, 579—597).—The bulk of this paper has but little chemical interest. Cardiac activity was studied by the cardio-electrogram, and the causes of pulsus alternans are discussed. In glyoxylic acid poisoning, this symptom is pronounced. W. D. H.

Union Relationships of Heart Muscle and Digitalis. B. Schliomensun (*Arch. exp. Path. Pharm.*, 1910, **63**, 294—302).—From the hearts of men and animals a group of substances can be isolated, namely, the alcohol-soluble phosphatides, which appear to have a special capacity to combine with the active material in digitalis. The corresponding fractions from the skeletal muscles and liver do not possess this property. It is not possible at present to say what are the definite chemical substance or substances that participate in this specific reaction. W. D. H.

The Formation in the Animal Body of *l*-β-Hydroxybutyric Acid by the Reduction of Acetoacetic Acid. Henry D. Dakin (*J. Biol. Chem.*, 1910, **8**, 97—104).—The liver contains not only an

oxydase which converts β-hydroxybutyric acid into acetoacetic acid, but also a reductase which produces the reverse change. The view taken of l-β-hydroxybutyric acid acidosis is that its main underlying cause is defective catabolism of acetoacetic acid. The conclusions are supported by experiments. The question is discussed whether the phenomena are due to the reversible action of one enzyme, or to the antagonistic action of two enzymes. The latter hypothesis fits in best with the facts. W. D. H.

The Degradation of Carboxylic Acids in the Animal Body. XII. A New Method of Formation of β-Hydroxybutyric Acid in the Animal Body. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, **27**, 474—490. Compare this vol., ii, 794, 795).—In experiments on perfusion of the dog's liver with ox-blood a fair amount of l-β-hydroxybutyric acid is formed, in most cases without the addition to the perfusing liquid of any substance which yields acetoacetic acid. If sodium acetoacetate is added to the perfusing blood, a large amount disappears, and from 42 to 62% of this is accounted for by the l-β-hydroxybutyric acid formed. If sodium butyrate, or especially *iso*-valerate, is added, there is a large formation of both acetoacetic and β-hydroxybutyric acids. Similar results were obtained in experiments with pounded liver substance. The agent which converts acetoacetic acid into l-β-hydroxybutyric acid is termed *keto-reductase*.

W. D. H.

The Decomposition of Acetoacetic Acid by Enzymes of the Liver. II. ALFRED J. WAKEMAN and HENRY D. DAKIN (*J. Biol. Chem.*, 1910, **8**, 105—108).—Further facts are given in relation to the liver reductase; the primary product of its action on acetoacetic acid is not acetic acid, but l-β-hydroxybutyric acid. W. D. H.

Uric Acid Metabolism in Dogs. H. ACKROYD (*Bio.-Chem. J.*, 1910, **5**, 217—224).—The liver of dogs when perfused with normal saline solution produces a small quantity of allantoin. When sodium urate is added to the perfusion fluid, a part of it is destroyed; part only of this is recovered as allantoin; no urea could be isolated. The dog's liver has not the power to destroy allantoin. W. D. H.

The Formation of Uramido-acids in the Organism. I. FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1910, **68**, 277—292).—The formation of uramido-acids in the body is important from the standpoint of urea formation, and former work on the question is quoted at length. The present experiments on the action of the dog's liver in the formation of such acids gave negative results. W. D. H.

Liver Pigments of Invertebrates. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1910, **28**, 56—59).—From the liver of invertebrates (molluscs being mainly used), two pigments were obtained, one soluble in water, the other in chloroform or alcohol. The former is rich in iron, and gives a continuous spectrum, the latter poor in, or free from, iron gives absorption bands. The same pigments are stated to be also obtainable from the vertebrate liver. W. D. H.

Study of Autolysis by Physico-chemical Methods. II. ROBERT L. BENSON and H. GIDEON WELLS (*J. Biol. Chem.*, 1910, **8**, 61—67. Compare *ibid.*, 1907, **3**, 35).—Autolysis is usually measured by the change in the amount of nitrogen contained in forms coagulable and not coagulable by heat, but it is shown by experiments with dog's liver, blood-serum, and blood that autolysis can be followed much more satisfactorily by freezing-point determinations supplemented by electrical conductivity measurements. Toluene was found to be the most satisfactory antiseptic in these experiments.

In agreement with Baer and Loeb (Abstr., 1905, ii, 734), the authors find that the inhibiting effect of serum on autolysis (the effect of dog serum on the autolysis of dog liver was observed) is scarcely affected by heating the serum at 85° or 95° for thirty minutes. In other cases, the inhibiting effect of serum appears to be diminished by heating, but there seems to be some discrepancy in the results obtained when the autolytic changes are measured by physical or chemical means, and when they are measured by the histological changes taking place in the cells. G. S.

The Occurrence of Free Guanosine in the Pancreas. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Biochem. Zeitsch.*, 1910, **28**, 127—130).—The separation of guanylic acid from the pancreas was found to be difficult, owing to the presence of guanosine, which is regarded as being in the free state. In fact it is sometimes more abundant than the acid. W. D. H.

Ethyl Acetate Extracts of Organs and their Behaviour in Autolysis. IV. and V. KENRO KONDO (*Biochem. Zeitsch.*, 1910, **27**, 427—435, 436—441. Compare this vol., ii, 791).—The present experiments with kidney, spleen, and blood were carried out in the same way as in previous work on the liver. The results with kidney and spleen (to some extent) were very similar, and there appears to be present in these organs substances other than cholesterol containing hydroxyl groups, the quantity of which increases in the warm. In the case of the blood, there was no evidence of any enzyme either in the corpuscles or plasma capable of splitting cholesterol esters. The acetyl number remains unchanged after autolysis. This is not due to the presence of an inhibiting agent, for the increase occurs when liver extract is added. W. D. H.

Formation of Oxalic Acid in the Organism. HERMANN JASTROWITZ (*Biochem. Zeitsch.*, 1910, **28**, 34—47).—Oxalic acid can arise from uric acid, aminodicarboxylic acids, and carbohydrates. In intermediate metabolism, it is formed especially in the spleen, and probably also in the liver and muscles (in dogs). In anomalies of nuclein metabolism (gout, leucæmia), increased oxalic acid formation occurs very seldom, but it may occur in diabetes. W. D. H.

Metabolic Disturbances after the Extirpation of both Suprarenal Glands. OSWALD SCHWARZ (*Pflüger's Archiv*, 1910, **134**, 259—288).—The animals used were rats; when both the suprarenals

are removed, the hepatic glycogen is much reduced or disappears entirely; this is regarded, not as due to general marasmus, but as a specific effect of the operation; when then fed on bread, glycosuria is produced; with feeding on pure dextrose, the glycogen returns in some measure to the liver. The administration of lævulose leads neither to glycogen formation nor to lævulosuria; it is apparently completely utilised in the body; feeding on sucrose leads to glycogen formation in virtue of its dextrose component; after feeding on starch, alanine, or aspartic acid, the liver is free from glycogen. Phloridzin is highly toxic to these animals; it produces glycosuria; they are also sensitive to adrenaline injections. A sugar mobilising function is assigned to adrenaline. W. D. H.

Toxic Action of Compounds on Isolated Muscle Regarded as a Chemical Change. VICTOR H. VELEY (*Quart. J. Exper. Physiol.*, 1910, **3**, 233—240).—From the experiments previously recorded by the author (mainly in conjunction with Waller, this vol., ii, 55, 228, 331, 524), the conclusion is drawn that living muscular tissue behaves as if it contained, not only proteins as such, but even their products of decomposition or hydrolysis, or, in other words, the living muscle behaves like a lifeless chemical reagent; the results obtained are not greatly inferior in accuracy to those obtained in reactions between highly refined chemical compounds under rigid physical conditions.
W. D. H.

The Quantitative Relations of Diastase in Different Organs of Different Animals. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, **27**, 385—396).—In estimating the diastase, Wohlgemuth's method and notation are employed. The pancreas, spleen, liver, blood, kidney, and other organs of various mammals, birds, fishes, and amphibians were investigated. The pancreas in all cases contains most diastase; the blood and liver generally come next; in rats on a starch diet, the diastase value of the pancreas rises from 300 to 400-fold. W. D. H.

Presence of Glycuronic Derivatives in Beef Bouillon. LÉON GRIMBERT and E. TURPAUD (*J. Pharm. Chim.*, 1910, [vii], **2**, 289—292). —The presence of reducing substances in aqueous extracts of beef has long been known, and the action has been variously ascribed to dextrose, maltose, *iso*maltose, pentoses, or glycuronic acid.

The author finds that bouillon, defaecated by mercuric nitrate solution, or boiled with hydrochloric acid, yields with phenylhydrazine a mixture of phenylglucosazone and phenylglycurosazone (Grimbert and Bernier, this vol., ii, 163). Glycuronic derivatives can also be detected by Tollens' reagent in bouillon defaecated by mercuric acetate, and from which the dextrose has been eliminated by the action of *Bacterium coli*. T. A. H.

Manganese of the Tissues of Lower Animals. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1910, **8**, 237—250. Compare Abstr., 1907, ii, 567).—Analyses of the amount of manganese in the different parts of various mussels are given. It is not regarded as merely adventitious; it is constantly present, and in spite of the small amount

present in the muscular tissue (which has a low order of activity in these animals), probably plays a rôle in respiration. In lakes poor in manganese (and poor also in the *Crenothrix* and diatoms which contain large amounts of manganese and form the food of the mussels), mussels cannot live. W. D. H.

Alcohol-Oxydase in Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1910, **28**, 145—168).—*Alcohol-oxydase* (alcoholase) is an enzyme which acts chiefly on ethyl alcohol, and converts it into acetic acid by absorption of molecular oxygen; aldehyde is an intermediate product; it also oxidises aldehyde directly. The enzyme does not decrease in amount in the tissues one or two days after death. It is most abundant in the liver, especially of the horse; the amount in human liver is relatively small; the kidneys also contain it, but the amount in other organs is very small. It acts neither in acid nor in strongly alkaline media; it acts best in faintly alkaline media. Addition of spleen to the liver increases the effect. Hydrogen peroxide has no effect. W. D. H.

Further Investigations on the Use of Silk Peptone for the Detection of Peptolytic Enzymes. EMIL ABDERHALDEN and EUGEN STEINECK (*Zeitsch. physiol. Chem.*, 1910, **68**, 312—316).—Details are given in regard to the best methods for obtaining silk peptone. Slices of organs (for instance, kidneys) placed in the peptone solution become, if a peptolytic enzyme is present, covered with tyrosine crystals. Whether healthy and pathological organs vary in this direction is to be further investigated. In the developing chick, peptolytic enzymes appear in the tissues at seventh to eighth day of incubation; in the pig embryo, in nearly all the tissues after the thirty-seventh day of development. W. D. H.

Enzymatic Acceleration of Cannizzaro's Aldehyde Transformation by Tissue Extracts. I. JAKOB PARNAS (*Biochem. Zeitsch.*, 1910, **28**, 274—294).—Animal tissues usually contain both fatty acid and the corresponding alcohol, and it is suggested that these are both derived from aldehyde by the Cannizzaro transformation. The liver, but not the lungs, contains a soluble ferment which accelerates this transformation, so that it takes place with aldehydes which otherwise tend to undergo aldol condensation. Quantitative production of the corresponding acid and alcohol was obtained from *n*- and *iso*valeraldehydes, *iso*butaldehyde, and propaldehyde, also from heptaldehyde after three hours' action of pig or ox liver. Benzaldehyde yielded a small quantity of alcohol; salicylaldehyde was not attacked. The name *aldehydemutase* is proposed for the enzyme. E. F. A.

Enterolipase. B. C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1910, **68**, 400—415).—As Lombroso showed, a mixture of bile and oleic acid stimulates the secretion in the intestine of a juice rich in lipase. Oleic acid alone has no such effect. Bile alone has not so great an effect as the mixture. These experiments were made with intestinal

loops. *In vitro*, the addition of bile increases the lipolytic action of the juice. Soap solution causes the secretion of a feebly lipolytic juice; *in vitro*, soap inhibits lipolytic action, but a small addition of alkali increases it. The addition of bile acids to bile increases its power of stimulating the secretion of lipase, and the effect of the mixture of bile and oleic acid is probably due to the bile acids. The group in the bile acid molecule to which this is due is to be the subject of renewed investigation. W. D. H.

Occurrence of Serine in Human Perspiration. GUSTAV EMBDEN and HERMANN TACHAU (*Biochem. Zeitsch.*, 1910, **28**, 230—236).—Hitherto only two nitrogenous substances, carbamide and ammonia, have been isolated from perspiration. From fresh perspiration, fairly large quantities of serine are now isolated by means of β-naphthalene-sulphonic acid. This method is advantageous in separating serine from the mixture of protein decomposition products obtained by acid hydrolysis. E. F. A.

The Production of Glycosuria in Relation to the Activity of the Pancreas. IVOR L. TUCKETT (*J. Physiol.*, 1910, **41**, 88—144).—Glycosuria due to anæsthesia and operation is probably not influenced by the pancreatic factor; neither is there evidence that the carbohydrate in the diet stimulates the pancreas to an increase in its internal secretion. Glycosuria following fistula or ligature of the thoracic duct is probably due to the anæsthetic employed and to disturbance of nerves, but as the internal secretion of the pancreas finds its way into the circulation by this duct, that may possibly be a subsidiary factor. The glycosuria associated with morphine and ether narcosis is the result of the rapid production of sugar from hepatic glycogen, other carbohydrates in the body, and also from fat. The sugar in the blood of cats exhibiting experimental glycosuria has a reducing power equal to that of dextrose. W. D. H.

Nature of Bence-Jones Protein. OWEN T. WILLIAMS (*Bio.-Chem. J.*, 1910, **5**, 225—229).—The protein was obtained in the urine of a case of myeloma; it is shown that it varies in composition from time to time even in the same case, and probably the true explanation lies in the fact than in the disintegration of bones and tendons, chondro-mucins are liberated, which are more or less broken up, and thus excreted differently according to the stage of the disease. The protein in the present case gave the typical reactions of the Bence-Jones protein. It resembles mucoid in that it contains a carbohydrate radicle and a high percentage of sulphur. The latter, however, varies, and when it sinks the amount of ethereal sulphate in the urine rises. W. D. H.

Diastase in the Blood and Urine of Rabbits. GOICHI HIRATA (*Biochem. Zeitsch.*, 1910, **28**, 23—28).—In experimental nephritis in rabbits, the diastase in the urine sinks; this is regarded as due to lessened functional activity of the kidney cells, and the decrease is greatest in cases where the injury is greatest. The rise of diastase in

the blood which accompanies this is regarded as due to defective elimination by the kidneys. W. D. H.

Metabolism in Addison's Disease. H. BEUTTENMÜLLER and FELICITAS STOLTZENBERG (*Biochem Zeitsch.*, 1910, **28**, 138—144).—In the case of Addison's disease investigated there was no important departure from the normal in nitrogen metabolism; on an abundant diet, the patient retained nitrogen; the administration of adrenal tablets had no effect. W. D. H.

The Excretion of Creatine in Diabetes. R. A. KRAUSE (*Quart. J. Exper. Physiol.*, 1910, **3**, 289—296).—A full account of experiments already published as a preliminary communication (see Krause and Cramer, this vol., ii, 793). W. D. H.

Prophylaxis in Malaria. Action of Small Continuous Doses of Quinine on the Development of the Animal Organism and its Application in Infectious Disease. ALBERT GRAZIANI (*Arch. Hygiene*, 1910, **73**, 39—80).—Injection of quinine hydrochloride for one hundred days in doses of 0·005 gram per kilo. of body-weight in young rabbits and guinea-pigs delays growth, and in adult animals lessens their weight. There is no change in the corpuscles or hæmoglobin of the blood; the bactericidal power of the lungs or of the serum is unaltered; so also are the opsonic index and the agglutinating action of the blood in reference to typhoid bacilli; in fact, in most cases the immunising power of the blood is diminished. The animals which had received quinine are much less resistant towards infection (typhoid, anthrax, cholera, pneumonia) than the control animals. Observations on the blood of man show the same results, and the conclusion is drawn that the same loss of resistance occurs in man also. W. D. H.

Atoxyl. IV. FERDINAND BLUMENTHAL (*Biochem. Zeitsch.*, 1910, **28**, 91—96. Compare Abstr., 1909, ii, 255).—The use of atoxyl preparations and of its various iodine and bromine derivatives in syphilis is suggested. The present experiments are mainly on animals to discover the relative toxicity of these compounds; the silver salts are less poisonous than those of mercury. W. D. H.

Absorption of Hydrogen Chloride by Animals. KARL B. LEHMANN and ARTHUR BURCK (*Arch. Hygiene*, 1910, **72**, 343—357).—In tracheotomised rabbits, the amount of hydrogen chloride absorbed in the first hour varied between 58 and 80% of the amount inspired; higher figures were obtained when the gas was given through the nose. The absorption increases with the depth of respiration. In the second hour there was no marked falling off in the rate of absorption; experiments lasting more than two hours were not made. W. D. H.

Absorption of Chloroform, Carbon Tetrachloride, and Tetrachloroethane in Animals and Man. KARL B. LEHMANN and HASEGAWA (*Arch. Hygiene*, 1910, **72**, 327—342).—The experi-

ments on two men were carried out by estimating the chloroform in the inspired and expired air, the difference giving the amount absorbed. In periods of five to ten minutes from 53 to 73% of the chloroform given was absorbed. In experiments for longer periods, the amount absorbed was greatest in the first five minutes, and then gradually declined. In rabbits the same falling off was noticed, but the total absorption was less than in man. Administration was either made by the nose or by the tracheal tube, but the method made no difference. Similar figures (in rabbits) were obtained with carbon tetrachloride and tetrachloroethane. W. D. H.

Influence of Gases on the Organism. XV. Hydrogen Arsenide. L. O. DUBITZKI (*Arch. Hygiene*, 1910, **73**, 1—38).—This gas was estimated in the air volumetrically either by calcium chloride, silver nitrate, or potassium iodate. In cats, 0·005% is fatal in sixty to ninety minutes, 0·004% in three hours. A prominent symptom is hæmolysis leading to hæmoglobinuria. The absolute fatal dose varies from 8·7 to 13·7 milligrams. W. D. H.

Action of Radium Emanations on the Development of Animal Eggs. II. OSCAR HERTWIG (*Sitzungsber. K. Akad. Wiss., Berlin*, 1910, **39**, 751—771).—Experiments on various eggs confirm the author's previous conclusions. The main interest of the paper relates to the action of the radium emanations on the sperm of the frog. After exposures varying from five minutes to twelve hours, the spermatozoa becomes more or less altered, but the nucleus is the most affected. These spermatozoa are still capable of fertilising the eggs, although development is slow in cases of long exposure and abnormal embryos are formed. This is regarded as an additional proof that the nuclear substance is the most important part of the male cell in fertilisation. W. D. H.

Action of Radium Bromide on the Skin of the Rabbit's Ear. J. O. WAKELIN BARRATT (*Quart. J. exper. Physiol.*, 1910, **3**, 261—270). —A disk of radium bromide placed on the ear of the rabbit produced a ring of pigmentation corresponding with the edge of the disk. Within the ring more or less depigmentation occurred. The deposit of pigment took place chiefly in the epidermis. In albino rabbits and with human skin no such effects were observed.

W. D. H.

The Pharmacological Action of Uranium. D. E. JACKSON (*Amer. J. Physiol.*, 1910, **26**, 381—395).—The action of uranium is generally believed to resemble that of cyanides, but there are many points of difference. Intravenously administered as the sodium uranium tartrate there is no increase in the flow of lymph from the thoracic duct even in lethal doses. The rise of arterial pressure is much more pronounced than that produced by cyanides, and the stimulating action on respiration is less marked. Blood coagulation is prevented, probably by union of the metal with one or more of the protein factors in the process. Further, there is no change in the hæmoglobin. Cyanides hinder the guaiacum reaction with extract of potato peelings; uranium does not. W. D. H.

Behaviour of Iodoso-, Iodoxy-, and Iodonium Compounds in the Animal Organism. II. Behaviour of Iodoxybenzene. RICCARDO LUZZATTO and G. SATTA (*Arch. Farm. sper. Sci.*, 1910, 9, 241—253. Compare this vol., ii, 433).—Even in quantities five times greater than the toxic dose of iodosobenzene, iodoxybenzene does not cause death in dogs, rabbits or frogs. The effects it produces are similar in kind to those of the former substance, but its action is much weaker and slower. It is converted in the organism into iodobenzene, for iodophenylmercapturic acid can be isolated from the urine, and its lower toxicity is probably due to the fact that this reduction occurs more easily than in the case of iodosobenzene. Iodoxybenzene does not exhibit any curare-like action on frogs.

R. V. S.

The Behaviour of β-p-Hydroxyphenyl-α-lactic Acid and p-Hydroxyphenylpyruvic Acid in the Surviving Liver. ERNST SCHMITZ (*Biochem. Zeitsch.*, 1910, 28, 117—120).—Neubauer and Falta have shown that those aromatic substances the ring of which is easily burnt in the body are excreted in alcaptonuria as homogentisic acid, whereas those which are not, or only with difficulty, broken up have no such influence on the excretion of homogentisic acid. Embden, Salomon, and Schmidt have shown that the former group leads in the isolated liver to formation of acetoacetic acid, whereas the latter does not. In the present experiments on liver perfusion this is confirmed; β-p-hydroxyphenyl-α-lactic acid does not yield homogentisic acid, and leads to a negligible formation of acetone substances in the liver; p-hydroxyphenylpyruvic acid leads to homogentisic acid formation in alcaptonurics and to an abundant formation of acetone substances in the surviving liver.

W. D. H.

Chemical and Physiological Properties of Triphenylstibine Sulphide. Behaviour of this Substance in the Animal Body. LUDWIG KAUFMANN (*Biochem. Zeitsch.*, 1910, 28, 67—86, 86—90. Compare Abstr., 1908, i, 1031).—Triphenylstibine sulphide has the power to produce the evolution of oxygen from hydrogen peroxide and other peroxides; the sulphur is split off and oxidised to sulphuric acid, whilst the residue is oxidised to antimony oxide or hydroxide and precipitated as sulphate by the sulphuric acid. The reaction runs quantitatively at a temperature of 36—37°. The sulphite is one hundred times more active than ordinary sulphur.

The therapeutic use of the sulphide in cases (for instance, of skin disease) where sulphur is usually employed appears from a few preliminary observations and experiments to be justifiable.

W. D. H.

Chemical Structure and Sympathomimetic Action of Amines. GEORGE BARGER and HENRY H. DALE (*J. Physiol.*, 1910, 41, 19—59).—The action of adrenaline on the sympathetic is termed sympathomimetic, and is also shown by a large series of amines, the simplest being primary fatty amines. The action increases with approximation to adrenaline structure. The amines active in this way

are primary or secondary; the quaternary amines corresponding with the aromatic members of the series have an action like that of nicotine. The optimum carbon skeleton for sympathomimetic activity consists of a benzene ring with a side-chain of two carbon atoms, the terminal one bearing the amino-group. Another optimum condition is the presence of two phenolic hydroxyls in the 3 : 4 position relative to the side-chain; when these are present, an alcoholic hydroxyl still further intensifies the activity. A phenolic hydroxyl in the 1 position does not increase the activity. Catechol has no such activity. The methyl-amino-group, including adrenaline, reproduces inhibitory sympathetic effects more readily than motor effects; the opposite is true for the primary amines of the same series. Instability and activity show no parallelism in the series. W. D. H.

The Fate of *p*-Hydroxyphenylethylamine in the Organism. ARTHUR J. EWINS and PATRICK P. LAIDLAW (*J. Physiol.*, 1910, **41**, 78—87).—This amine is converted in part in the body into *p*-hydroxyphenylacetic acid; the surviving liver can effect this change, so also can the plain muscle of the uterus, but not that of the lung vessels. The isolated heart causes complete destruction of the amine. The amine is less readily converted into hydroxyphenylacetic acid than the primary amine, and hordenine, the tertiary base, still less readily than the secondary base. W. D. H.

The Behaviour of Veronal (Sodium Veronal) in the Animal Body, after One Administration, and in the Chronic Condition. C. BACHEM (*Arch. exp. Path. Pharm.*, 1910, **63**, 228—241).—After the subcutaneous injection of small doses of veronal, about 90% appears in the urine; in larger doses this sinks to 45—50% whether the drug is given in one or successive doses. The fæces contain only a small quantity, so about half is destroyed in the body, how or why is unknown. Small doses do not influence the well-being of the animals used. After three days, only small amounts are still found in the urine and organs. Its affinity for brain tissue is doubtless related to its narcotic properties. Even after large doses, a small fraction only is found in the stomach some hours later. In acute poisoning, the stomach must therefore be washed out early if it is to be of any avail. W. D. H.

The Prophylactic Action of Atropine in Immediate Anaphylaxis of Guinea Pigs. III. JOHN AUER (*Amer. J. Physiol.*, 1910, **26**, 439—452).—Guinea pigs sensitised by the subcutaneous injection of 1 to 2 c.c. of horse-serum reach their maximum sensitiveness about the ninth week, and this is then maintained for at least twenty-three weeks (the longest interval tested). Atropine was used as a prophylactic, as the symptoms of anaphylaxis are mainly due to contraction of bronchial muscles. Experimentally, atropine was found to be of distinct therapeutic utility. Without atropine, the death rate was 75%, with it only 28%. W. D. H.

The Clinical Application of Ergotamine (Tyramine). ALFRED CLARK (*Bio.-Chem. J.*, 1910, **5**, 236—242).—Tyramine given by the

mouth to a healthy subject in doses of 30 to 100 mg. causes a slight rise of blood-pressure which lasts some hours. When injected hypodermically (20 to 50 mg.), the rise is rapid and well marked, lasting about twenty minutes. When similarly given in cases of "shock," the blood-pressure rises slightly. W. D. H.

Action of Curarine and Allied Substances. RUDOLF BOEHM (*Arch. exp. Path. Pharm.*, 1910, 63, 177—227).—The direct excitability of skeletal muscle (frog) to induction shocks remains unaltered even by large doses of curarine, but the excitability varies in different parts. Towards condenser discharges, the effects are variable, as also they are in normal muscles. Muscles can easily be poisoned with curarine by immersing them in a solution of the drug. The great toxicity of the drug comes out when it is compared with other ammonium derivatives; the following relative figures are given: Choline, 0·35; tetraethylammonium, 0·125; trimethylethylammonium, 0·015; neurine, 0·012; tetramethylammonium, 0·005; muscarine, 0·0025; trimethylvalerylammonium (valearine), 0·001; curarine, 0·00001. W. D. H.

Elementary Action of Digitalis Substances. RUDOLF MAGNUS and (Miss) S. C. M. SOWTON (*Arch. exp. Path. Pharm.*, 1910, 63, 255—262).—Observations by the authors confirm Straub's views on the action of the digitalis group. The increased activity of the heart can be shown, not only in the intact animal, but also on the isolated heart. Illustrative experiments on the effect of strophanthin are given in full. W. D. H.

The Concentration of Ammonia in the Blood of Cats and Dogs necessary to Produce Ammonia Tetany. CLARA JACOBSON (*Amer. J. Physiol.*, 1910, 26, 407—412).—Ammonium carbonate was injected intravenously, and the concentration in the blood found necessary to produce tetany is identical with the concentration of ammonia in the blood when tetany occurs as a result of removal of the parathyroids. In the latter condition the liver is depressed in its power to destroy ammonia. W. D. H.

Antimony Poisoning in Compositors. P. SCHRUMPF and B. ZABEL (*Arch. exp. Path. Pharm.*, 1910, 63, 242—254).—Various symptoms presented by compositors could not be attributed to lead poisoning, but are due to antimony; the blood conditions underlying this are a slight leucocytosis, but a great excess of eosinophile cells. Similar conditions can be produced artificially by antimony in rabbits. No drug treatment is suggested; mere cessation of work in the men; or cessation of antimony dosage in animals, leads rapidly to a return to normal conditions. W. D. H.

The Comparative Toxicity of Theobromine and Caffeine as Measured by their Direct Effect upon the Contractility of Isolated Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. Roy. Soc.*, 1910, 82, *B*, 568—574).—Caffeine produces con-

tracture and finally abolition of contraction in muscle. With caffeotannic acid the admixture with tannic acid retards the change. Theobromine causes a similar effect, its toxic value compared with that of caffeine being 1·7 : 1 for equal molecules, or 1·8 : 1 for equal weights. The introduction of the methyl group into theobromine to form caffeine lowers the toxicity, a result converse to that found in certain other organic compounds. Experiments are also recorded with extracts of tea and coffee; "caffeine-free" coffee has but little action.

W. D. H.

The Relationship of Surface-tension to the Union of Toxin and Anti-toxin. AMILCARE BERTOLINI (*Biochem. Zeitsch.*, 1910, **28**, 60—66).—Traube stated that toxins in opposition to anti-toxins lower the surface-tension, and that the union of toxin and anti-toxin has a still greater effect than the toxin. The present investigations made with diphtheria and tetanus toxin and anti-toxin do not confirm this view. The union has no effect on surface-tension as tested by Traube's stalagmometer.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Apparatus for Collecting and Measuring the Gases Evolved During Fermentation. ARTHUR HARDEN, J. THOMPSON, and WILLIAM J. YOUNG (*Bio.-Chem. J.*, 1910, 5, 230—235).—In measuring the total quantity and rate of evolution of gases evolved during fermentation, it is essential to keep the pressure in the flask as nearly constant as possible throughout the experiments.

Two forms of apparatus devised and used by the authors for this purpose are fully described with diagrams. W. D. H.

Influence of the Mineral Constituents of Nutritive Solutions on the Development of Azotobacter. (Mme.) H. KRZEMIENIEWSKA (*Bul. Acad. Sci. Cracow*, 1910, *B*, 376—413).—Potassium, calcium, magnesium, phosphorus, and sulphur are all essential to the development of *Azotobacter*. Under the conditions of the experiments, the minimum amounts required for the normal consumption of 1 gram of dextrose were as follows: K, 0·38 ; Ca, 0·36 ; Mg, 0·35 ; P, 2·46 ; and S, more than 0·49 mg. Deficiency of any essential mineral constituent of the nutritive solution results in the less economical utilisation of the dextrose, and consequently less nitrogen is fixed per gram of dextrose. The organisms leaves off increasing, whilst the respiration of the existing cells goes on.

The addition of potassium, sodium, and magnesium compounds above certain limits acts injuriously on *Azotobacter*. The injurious effect is diminished or prevented by addition of calcium salts. Addition of magnesium salts lessens the injurious action of excessive amounts of potassium and sodium. N. H. J. M.

Assimilation of Nitrogen by Certain Nitrogen-fixing Bacteria in the Soil. W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1910, *B*, **82**, 627—629. Compare *ibid.*, **81**, 287)—Culture solutions inoculated respectively with pure cultures of *Azotobacter* from garden soil, and *Pseudomonas* from bean and clover nodules and with both organisms together, showed that whilst *Azotobacter* alone fixed 2·19 mg. and *Pseudomonas* alone 2·30 mg. of nitrogen per unit of carbohydrate, the two organisms together fixed 4·51 mg. per unit of carbohydrate.

Further experiments are described in which garden soil (5 oz.), both without and with lime, was inoculated from an extract of soil which had been sterilised and then inoculated with *Azotobacter* and *Pseudomonas* so as to accustom the organisms to soil conditions. In ten days the mixed culture in limed soil gave an increase of 35 mg. of nitrogen, and in the unlimed soil an increase of 25 mg. The amount of nitrogen introduced by the culture itself was 6 mg. N. H. J. M.

Some Factors Concerned in the Fixation of Nitrogen by Azotobacter. CONRAD HOFFMANN and B. W. HAMMER (*Centr. Bakt. Par.*, 1910, ii, **28**, 127—139).—Experiments with a number of different soils showed that their nitrogen-fixing power varied from 0·15 to 14·47 mg. of nitrogen per gram of mannitol consumed.

Mannitol and lactose proved to be the best sugars for maximum fixation in impure cultures, whilst very little fixation was obtained with maltose and sucrose. With pure cultures, mannitol and dextrin gave the best results, and good results were also obtained with sucrose, but not with lactose.

As regards mineral nutrients, di- and tri-calcium phosphates give better results (in impure cultures) than the monocalcium salts.

The period of incubation for impure cultures should be from twenty-one to twenty-eight days. If too prolonged, losses of nitrogen may occur. Calcium carbonate need only be present in very small amounts.

The amount of protein in the cells of *Azotobacter* was found to range from 8·31 to 19·13%, whilst the phosphorus (as P_2O_5) varied from 2·51 to 2·97%. N. H. J. M.

The Products Resulting from the Putrefaction of Fibrin by Clostridium carnofœtidus, and the Rauschbrand Bacillus. FRANCIS H. McCRUDDEN (*J. Biol. Chem.*, 1910, **8**, 109—114).—The two micro-organisms mentioned are selected as widely different types of anaërobes. The products of putrefaction of fibrin show distinct differences, Rauschbrand leading, for instance, to the formation of about one-fifteenth of the gases produced by *Clostridium*. The question is to be followed up in the hope that such differences may be of diagnostic value. W. D. H.

Action of Dysentery Bacilli on Nitrites and Nitrates. W. J. LOGIE (*J. Hygiene*, 1910, **10**, 143—154).—All the dysentery strains examined with one exception (*B. Neisser*, Ac.) reduced nitrates to nitrites; none which fail to ferment mannitol destroyed nitrites. *B. dysenteriae*, Jürgens, although closely related to *B. dys.*, Flexner, differs from

it in its action on litmus whey, and in failing to destroy nitrite. *B. dys.*, Jürgens, is the only strain found to form indole, and, therefore, to give the cholera-red reaction. The addition of dextrose enables Shiga strains to destroy nitrites. With an abundant supply of oxygen, all the strains fail to destroy nitrites and nitrates, but in media which contain dextrose the inhibitory effect of oxygen is less marked. Under anaërobic conditions, Shiga strains and *B. dys.*, Jürgens, still fail to destroy nitrites. W. H. D.

The Enzymes in Different Bacteria. EMIL ABDERHALDEN, LUDWIG PINCUSSOHN, and ADOLF R. WALTHER (*Zeitsch. physiol. Chem.*, 1910, **68**, 471—476).—The culture fluids of a paratyphoid-like bacillus and of *Streptococcus pleuro-pneumoniae* have no peptolytic action on various kinds of peptone. *Paratyphus B.* slightly decomposes casein peptone. Various bacilli were grown in different media with and without peptone, and the change in the rotatory power noted. It is hoped that this method, of which a few preliminary examples are given, may be utilised in the differentiation of micro-organisms.

W. D. H.

Amount of Phosphorus in Yeast and in Some Yeast Preparations. EDUARD BUCHNER and HUGO HAEHN (*Biochem. Zeit.*, 1910, **27**, 418—426).—Yeast which had been subjected to a pressure of 70 atmospheres was found to contain about two-thirds of the total phosphorus originally present.

Yeast prepared with acetone contains more phosphorus than when acetone and ether are employed. No connexion seems to exist between the fermenting power of yeast and the percentage of phosphorus.

N. J. H. M.

Action of Sodium Selenite on the Production of Carbon Dioxide from Living and Dead Yeast. MARIE KORSAKOFF (*Ber. deut. bot. Ges.*, 1910, **28**, 334—338).—Whilst a 1% sodium selenite solution completely checks the production of carbon dioxide from zymin, living yeast produces considerable amounts even in 30% solutions. Small amounts of sodium selenite (0·1—0·5%) even increase the activity of living yeast. N. H. J. M.

Fermentation of Galactose by Yeast and Yeast Juice. ARTHUR HARDEN and ROLAND V. NORRIS (*Proc. Roy. Soc.*, 1910, *B*, **82**, 645—649).—The results of other investigators showing that some yeasts when cultivated in a medium containing galactose acquire the property of fermenting galactose are confirmed. Yeast trained in this manner yields a juice capable of fermenting galactose.

A fermenting mixture of yeast juice and galactose reacts with phosphate in a manner similar to yeast juice and dextrose. The rate is accelerated; an extra amount of carbon dioxide is evolved, equivalent to the phosphate added, after which the rate again becomes normal. An organic phosphorus compound is produced, which is not precipitated by magnesium citrate mixture. Small amounts of sodium arsenate also accelerate the fermentation of galactose. N. H. J. M.

Disinfection by Chemical Agencies and Hot Water. HARRIETTE CHICK (*J. Hygiene*, 1910, **10**, 237—286).—Further experiments are adduced to show that disinfection is an orderly time process analogous to a chemical reaction between the bacterium and the disinfectant. The destruction of bacteria by water between 45° and 55° is also a consistent time process, and runs parallel to the heat coagulation of proteins; both proceed in accordance with the mass-law and in agreement with the law of Arrhenius in relation to temperature changes. The temperature-coefficient is very high. Disinfection by drying and by sunlight, so far as can be judged by the scanty data at present available, fall into line also. A large number of different micro-organisms were subjected to experiment.

W. D. H.

The Influence of Cell Lipoids on the Autolysis of Wheat Seedlings. MARIE KORSAKOFF (*Biochem. Zeitsch.*, 1910, **28**, 121—126). —Powdered wheat seedlings were allowed to autolyse, and the amount of proteolysis was estimated; previous extraction of the powder with solvents of lipoids (light petroleum, ether, alcohol, etc.) lessens the amount of autolysis, from which the conclusion is drawn that they have an important influence on the process. W. D. H.

Rôle of Reduction Processes in the Respiration of Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1910, **28**, 319—329).—The reducing power of various seeds, as indicated by methylene-blue, was found to be greatest in peas and least in cereals and oil seeds, whilst wheat and lupins occupy an intermediate position. There is a certain parallelism between the anaerobiose and the reducing power of seeds, since the anaerobiose is highest in leguminous seeds and lowest in cereal and oil seeds (Godlewski and Polzeniusz, Abstr., 1898, ii, 400; 1901, ii, 618).

Acid salts, such as dihydrogen potassium (or sodium) phosphate, depress the reducing power of pea seeds. Neutral salts and sodium selenite and ammonium vanadate act still more unfavourably. Alkalis, and especially dibasic phosphates, stimulate the reduction process.

N. H. J. M.

Action of Salts on the Respiration of Plants and on the Respiration Enzymes. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1910, **27**, 450—473).—All the salts contained in Knop's nutritive solution depress the energy of respiration. An acid reaction is especially injurious, and alkalis also cause a decrease.

Dibasic phosphates considerably increase the production of carbon dioxide in ground living seeds of *Pisum sativum*, *Zea Mais*, and *Lupinus angustifolius*, and in the seeds frozen and killed with acetone. In the case of *Triticum* the energy of respiration was diminished.

Acid phosphates diminish the production of carbon dioxide. Only basic phosphates have a stimulating effect. Phosphates stimulate not only the zymase, but also the oxydases, catalases, and reductases.

As regards the relative amounts, or the relative activity of the reductase and catalase of different seeds, it was found that the activity

of the reductase increased in the following order: *Zea* (0), *Triticum* (1), *Lupinus* (10), and *Pisum* (480), whilst in the case of catalases the order is reversed: *Pisum* (10), *Lupinus* (12), *Triticum* (30), and *Zea* (50). N. H. J. M.

Importance of Mucilages in the Germination of Seeds. CIRO RAVENNA and M. ZAMORANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 247—252).—Linseed which has been deprived of its mucilage by repeated treatment with water yields fewer seedlings than the untreated seed, and their weight and ash are less than that of normal seedlings. When, however, the sand in which germination is effected is treated with a solution containing sugar and the inorganic constituents found in the mucilage extracted, the weight and ash of the seedlings obtained approximate to those of normal seedlings. This tends to show that the mucilage functions as a reserve food material during germination. R. V. S.

Lecithin and Lecithides in Germinating Seeds. LUIGI BERNARDINI and G. CHIARULLI (*Bied. Zentr.*, 1910, **39**, 594—596; from *Staz. sper. agrar. ital.*, 1909, **42**, 97).—Seeds of cereals contain both free and combined lecithin in the proportion of about 1:2. During normal germination both forms of lecithin increase, at about the same rate, until the period of chlorophyll production, after which it decreases. In absence of light, germination is accompanied by a loss of lecithin, chiefly of the combined portion. N. H. J. M.

Occurrence and Detection of Chlorogenic Acid in Plants. Extraction and Yield of Caffeic Acid from Plants. CHARLES CHARAUX (*J. Pharm. Chim.*, 1910, [vii], **2**, 292—298).—From Gorter's results (Abstr., 1908, i, 186, 345) it appears that caffeic acid in plants results from chlorogenic acid, and the author has therefore devised a quantitative method of extracting caffeic acid from plants, and from the results so obtained he proposes to deduce the quantity of chlorogenic acid present, on the assumption that the latter is equivalent to about half its weight of caffeic acid.

The residue left on distilling the solvent from an alcoholic extract of the finely-ground plant is taken up with warm water and this shaken out twice with ether to remove impurities. The filtered aqueous extract is treated with excess of a solution of basic lead acetate, the precipitate collected, washed, and decomposed with cold dilute sulphuric acid in slight excess, giving a solution of impure chlorogenic acid. This is rendered slightly alkaline, boiled for thirty minutes, and excess of dilute sulphuric acid added. The liberated caffeic acid is extracted with ether, purified by re-crystallisation from boiling water, and weighed. In some cases it requires further treatment for the removal of impurities. A number of colour reactions for the detection of chlorogenic acid are given, and a list of plants in which this acid has been found and estimated as caffeic acid by the process outlined above. The quantity of caffeic acid found varied from 0·6 to 10% for different plants. T. A. H.

Rôle of Catalase in Plants. ANNA ROSENBERG (*Ber. deut. bot. Ges.*, 1910, **28**, 280—288).—Results of experiments with a variety of seeds in which equal weights of the powdered substance were digested for an hour with water and treated with hydrogen peroxide indicated that no direct connexion exists between the anaerobiose and the catalase, since the leguminous seeds acted the least on hydrogen peroxide, whilst the cereal seeds, although little suited to anaerobiose, proved to be very rich in catalase.

Acids, even 0·25% citric acid, are very injurious to catalase, and the acid phosphates of sodium and potassium decrease its activity. Alkali salts, such as sodium carbonate and dibasic phosphates, are favourable, the latter acting most in the case of seeds which only contain small amounts of catalase.

The catalase of lupins is rapidly destroyed by autolysis. Addition of dibasic phosphates protects the catalase from decomposition; the amount, however, gradually diminishes when the temperature is raised.

Whilst the amount of catalase increases during germination, addition of potassium nitrate, magnesium sulphate, potassium dihydrogen phosphate, and calcium nitrate respectively (0·5%) was found to retard the production of catalase. N. H. J. M.

Alkaloidal Content of Cinchona Leaves. P. VAN LEERSUM (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 210—227).—The researches of Junghuhn, de Vrij (Abstr., 1897, i, 383), Broughton, Howard and Moens have shown on the whole that cinchona leaves contain alkaloids, although they leave some doubt as to the existence of other than amorphous alkaloids in these plant organs. Lotsy's physiological experiments with cinchona leaves (*Ann. Jard. Bot. Buit.*, 1899, **12**, 36) indicated that alkaloids are formed in the leaves, whence they are transported to the stem, where the final formation of crystalline alkaloids occurs, and hence are to be regarded as assimilation products. The present paper disproves Lotsy's contention, and shows that the alkaloids, which include quinine and cinchonine, occurring in the leaves are products of metabolism.

The method of estimating the total alkaloids consisted in mixing the ground leaves or bark with slaked lime, sodium hydroxide and ammonia, and extracting with ether, the alkaloids being recovered from the latter in the usual manner, dissolved in *N*/10-acid, and the excess of acid titrated. The results obtained show (1) that exposure of living leaves to light or dark has no effect on their alkaloidal content; (2) that no evidence could be obtained of the transport of alkaloid through the branches to the stem, and (3) that both the mesophyll and veins of the leaves of *C. Ledgeriana* and *C. succirubra* contain the crystalline alkaloids, quinine and cinchonine. These results are on the whole in harmony with those found for *Datura Stramonium* by Feldhaus (Abstr., 1905, ii, 648), and for tea by Du Pasquier (*Inaug. Diss.*, Zurich, 1908), and by Weevers (*Ann. Jard. Bot. Buit.*, 1904, 21, ii, Part 1), with the exception that Weevers found no caffeine in fallen tea leaves, whilst in the present investi-

gation fallen cinchona leaves proved to be as rich in alkaloids as the living leaves. T. A. H.

The Alkaloid of Pituri Obtained from Duboisia hopwoodii. A. C. H. ROTHERA (*Bio.-Chem. J.*, 1910, **5**, 193—206).—The alkaloid of pituri is nicotine; no evidence was found of the presence of any other alkaloid. W. D. H.

Action of Ultra-violet Rays on Plants Yielding Coumarin, and on Plants in which the Odour is due to Decomposable Glucosides. JEAN POUGNET (*Compt. rend.*, 1910, **151**, 566—569. Compare Heckel, this vol., ii, 63).—An odour of coumarin is rapidly developed when the leaves of plants, such as *Melilotus officinalis* or *Asperula odorata*, are exposed for a short time to the light from a quartz-mercury lamp. The leaves become blackened, owing to the death of the protoplasm; the enzymes survive, however, and effect scission of the glucosides. The action of ultra-violet light in this respect is identical with that of cold and anæsthetics (Grignard, Abstr., 1909, ii, 813; Mirande, *ibid.*, ii, 824).

Similar results have been obtained in experiments on the leaves of the cherry laurel and other plants which develop their characteristic odour on exposure to the rays. W. O. W.

Effect of Poisonous Solutions Containing Alkaloids on Soils and Plants. RICHARD OTTO and W. D. KOOPER (*Landw. Jahrb.*, 1910, **39**, 397—407. Compare *ibid.*, 1896, **25**, 1007).—Nicotine solutions (0·3%) are very favourable to the growth of *Nicotiana tabacum*, and favourable to *Solanum tuberosum*. In the case of *Nicotiana* the amount of alkaloid was increased, and similar results were obtained with other nitrogenous substances, such as sodium nitrate. The alkaloid had no appreciable effect on the other constituents.

Nicotine is absorbed physically by humus and sandy soils. It partly decomposes in the soil, with production of ammonia, and a part is lost by volatilisation. N. H. J. M.

Origin and Physiological Function of Pentosans in Plants. II. CIRO RAVENNA and O. MONTANARI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 202—207. Compare Ravenna and Cereser, Abstr., 1909, ii, 1046). —The results previously described have been confirmed in most respects by further experiments on the leaves of *Vicia faba minor*. The quantity of pentosans present in the leaves showed a tendency to increase during the day and decrease during the night. A considerable increase occurs when the leaves are supplied with carbohydrate food (dextrose, fructose, sucrose), whilst prevention of the function of the chlorophyll in the leaves and the absence of carbohydrate nutriment cause the amount of pentosans to decrease. R. V. S.

Chemico-physiological Investigations on the Tubercles of Vicia faba. GIOVANNI SANA (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 207—211).—In the fresh plant, the bacteroidal tissue of the tubercles was found to contain 0·965% of nitrogen, the cortical layer

only traces. In the roots, 0·2987% of nitrogen was found, in the stems, 0·1635—0·065%, and in the leaves, 0·707—0·7995%. The non-protein nitrogen in the tubercles amounted to 0·033%. Boiling water extracts various amino-acids from the tubercles; among them *l*-asparagine and glycine were identified. R. V. S.

Metabolism of Moulds. Aspergillus fumigatus. I. CIRO RAVENNA and G. PIGHINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 312—316).—From alcoholic extracts of three cultures of *A. fumigatus*, the authors isolated the following three substances respectively: (1) a highly toxic *substance*, forming colourless, prismatic crystals, m. p. about 300°; (2) mannitol; (3) trehalose. R. V. S.

Behaviour of Moulds Towards the Stereoisomerides of Unsaturated Dibasic Acids. ARTHUR W. DOX (*J. Biol. Chem.*, 1910, **8**, 265—267).—Buchner found that *Penicillium glaucum* and *Aspergillus niger* will grow in media containing ammonium salts of fumaric acid. But they were not able similarly to utilise maleic acid as a source of carbon. The latter is not found in nature; nevertheless, the distinction is surprising, because of the readiness with which the two acids are convertible one into the other. The present experiments, made with a large number of moulds, confirm Buchner's statement. Mesaconic and citraconic acids also resemble maleic acid. Itaconic acid gave a slight growth in a few cases, but no normal colony. W. D. H.

Amylase of Ungerminated Cereals and Malt. T. CHRZASZCZ (*Bied. Zentr.*, 1910, **39**, 641—642; from *Zeitsch. Spiritusind.*, 1909, **32**).—Malt amylase acts most favourably when 1% potato starch is employed with a temperature between 50° and 55°. The amylase of ungerminated cereals shows the same optimal temperatures for saccharification, but is less active than the amylase of malt. The diastatic power of wheat and rye is greater than that of barley, and still greater than that of oats. The assumption that malt has a special amylase, different from the amylase of resting grain, would therefore seem to be incorrect. It is probable that in cereals the action of the amylase is retarded by some unknown factor (amylum-coagulase).

It is suggested that cereal seeds contain an amylase which does not possess the full enzymatic power, a pro-enzyme which changes to active enzyme during germination. N. H. J. M.

Composition of Barbados Rain. R. RADCLYFFE HALL and J. R. BOVELL (*Rep. Agric. Work, Barbados; Imp. Dept. Agric. West Indies for* 1907–1909, 3. Compare Brünnich, this vol., ii, 647). —Analyses of fortnightly samples of rain-water from December, 1907, to May, 1909. The average amounts of nitrogen as ammonia and as nitrates in the rain of 1908, and the total amounts per acre, were as follows:

	Nitrogen per million		Nitrogen per acre (lb.)			Per cent. of Total N.	
Rainfall, inches.	as Ammonia.	as Nitrates.	as Ammonia.	as Nitrates.	Total.	as Ammonia.	as Nitrates.
40·28	0·032	0·384	0·295	3·498	3·793	7·8	92·2

The chlorine in the rain-water amounted to 8·38 per million, corresponding with 76·39 lb. per acre. N. H. J. M.

Analytical Chemistry.

A New Indicator for Alkalimetry and Acidimetry. 6-Sulpho-β-naphthol-1-azo-*m*-hydroxybenzoic Acid. R. MELLET (*Chem. Zeit*, 1910, **34**, 1073—1074)—When 4-amino-3-hydroxybenzoic acid is diazotised and combined with β-naphthol-6-sulphonic acid, a soluble dye is obtained, which may be used as an indicator.

The sodium salt forms dark violet crystals, dissolving readily in water to a violet solution. The acid is also soluble, and forms deep red solutions. Alkalis change the colour to violet, but an excess of alkali causes a change to cherry-red; the indicator is therefore unsuitable for use on test-papers. The indicator is prepared by adding *N*/10-hydrochloric acid to a 1% solution of the sodium salt until the colour is distinctly red. Such a solution is three times as strongly coloured as one of litmus of equal concentration. In *N*/100-solutions of acids or alkalis, the sensitiveness is equal to that of phenolphthalein. C. H. D.

Chart Presentation of Recent Work on Indicators. GEORGE S. WALPOLE (*Bio.-Chem. J.*, 1910, **5**, 207—214. Compare this vol., ii, 541).—The apparatus previously described is explained more fully, the new method of notation of hydrogen-ion concentration explained, and a diagram is given of how Sörensen's results can be conveniently displayed on a chart. A few examples illustrate how the chart may be used. W. D. H.

Apparatus for Measuring Known Quantities of Liquids. J. HUDIG and M. J. VAN'T KRUYS (*Chem. Weekblad*, 1910, **7**, 879—882).—Six vertical tubes closed by stopcocks at the lower end are sealed at their upper ends into a tube slightly inclined to the horizontal, connected at one end through a stopcock to a water pump, and at the other (lower) through a long vertical tube to the vessel containing the liquid to be measured. A short glass tube sealed into the main tube, and closed with rubber tube and a pinchcock, serves to admit air to the apparatus at will. The liquid is drawn up into the horizontal tube by the water pump, and flows into the vertical stopcock tubes. Definite volumes are marked on these tubes, aud can be measured off. The apparatus is specially adapted to the measurement of given volumes of strong acids. A. J. W.

Quantitative Spectral Analysis. WALTHER HEMPEL and RALPH L. VON KLEMPERER (*Zeitsch. angew. Chem.*, 1910, **23**, 1756—1759).—An arrangement is described by means of which certain metals can be quantitatively estimated by spectroscopic observations. The spectroscope is focussed on a oxyhydrogen flame

supplied with hydrogen and oxygen at constant pressure, and the metals are introduced into the flame by allowing the gases, evolved from an acidified solution of the metal by an electric current of constant strength, to mix with the entering hydrogen. The concentration of the solution under examination is diminished until the characteristic lines of the particular metal just cease to be recognisable in the spectroscope.

From comparative observations under exactly similar circumstances with a standard solution, the concentration of the metal in a solution of unknown strength can be obtained. The method can be applied to the estimation of potassium, lithium, calcium, and thallium, and is recommended for the estimation of the two former in samples of soil. It is shown that the presence of small quantities of other flame-colouring metals is without much influence on the results obtained. Larger quantities lead to an apparent diminution in the quantity of the metal under examination. H. M. D.

Volumetric Method of Estimating Iodide in Presence of Chloride, Bromide, or Free Iodine. William C. Bray and G. M. J. MacKay (*J. Amer. Chem. Soc.*, 1910, **32**, 1193—1204).—A method of estimating iodides in aqueous solution is described which is based on that suggested by Sammet (Abstr., 1906, ii, 153), and depends on the oxidation of the iodide by potassium permanganate, the removal of the liberated iodine with carbon tetrachloride, and its subsequent titration with standard sodium thiosulphate. Experiments have been made with potassium iodide solutions of known strength, which show that the results obtained by this method are accurate within 0·1%, and are independent of the presence of chlorides, bromides, or copper sulphate. When free iodine is present in the solution to be analysed, it is estimated by direct titration with sodium thiosulphate; the amount of iodine present as iodide is then ascertained by subtracting this quantity from the total iodine.

The estimation may be carried out by titrating the solution directly with potassium permanganate in presence of carbon tetrachloride, since, as the concentration of the potassium iodide is decreased, a larger proportion of the iodine is dissolved by the carbon tetrachloride, until finally the aqueous liquid becomes colourless. It has been found, however, that this method is not entirely satisfactory, since the reduction of the permanganate to the manganous salt is not quite complete, and an error amounting to about 0·4—0·5% of the permanganate solution is thus introduced. E. G.

Estimation of Fluorine in Aromatic Fluorine Derivatives. Hans Meyer and Alfred Hub (*Monatsh.*, 1910, **31**, 933—938).—See this vol., i, 735.

An Ozonometer. Stephan Jahn (*Ber.*, 1910, **43**, 2319—2321).—The ozonometer consists essentially of a U-tube fitted with stopcocks, one of these being a three-way one, and connecting with a manometer containing paraffin oil. The U-tube is 2 cm. in diameter, and has an internal volume of about 70 c.c.; sealed into it, and running

through its length, is a thin platinum wire, which can be heated by an electric current.

To use the instrument, 150—200 c.c. of the gaseous mixture containing ozone are passed through the U-tube, which is then closed at the inlet. The three-way tap is turned to connect with the manometer, and the liquid in the latter adjusted to a zero mark. The platinum wire is then heated to a dull red heat for five to ten seconds, this time being sufficient to destroy the ozone. When the original temperature has been attained, the manometer is again adjusted to zero, and the increase of pressure determined, from which the percentage of ozone can be calculated. A correction has to be applied for the amount of ozone decomposed while the gas is in contact with the cold platinum wire before the latter is heated. This is determined by a blank experiment.

The method is more exact and quicker than the determination of ozone with potassium iodide. T. S. P.

The Quantitative Analysis of Some Inorganic Sulphur Acids. Angelo Casolari (*Gazzetta*, 1910, **40**, ii, 22—27).—A polythionate containing m atoms of sulphur in the molecule yields $m-1$ molecules of sulphuric acid when treated with hydrogen peroxide and sodium or potassium hydroxide (Abstr., 1908, ii, 222). The solution to be titrated is therefore rendered perfectly neutral, and treated with a pure neutralised solution of hydrogen peroxide and a known volume of $N/10$-alkali hydroxide. After heating on the water-bath, the excess of alkali is titrated with acid: $Na_2S_mO_6 + (3m-5)H_2O_2 + (m-1)H_2O = Na_2SO_4 + (m-1)H_2SO_4 + (3m-5)H_2O$. The same reaction may be used for thiosulphates: $Na_2S_2O_3 + 4H_2O_2 + H_2O = Na_2SO_4 + H_2SO_4 + 4H_2O$. Under the same conditions, thiocyanates are decomposed into a sulphate and a cyanate: $KSCN + 4H_2O_2 + 2KOH = K_2SO_4 + KCNO + 5H_2O$. A volume of $N/10$-sulphuric acid equal to that of the alkali taken is then added, and, after boiling for a few minutes, the acidity of the solution is determined. If ammonium thiocyanate is present, the ammonia must be expelled by boiling with alkali before oxidising.

When a thiosulphate and a thiocyanate are both present in the solution, the sum of the two may be estimated as above, and the thiosulphate estimated separately by means of iodine. C. H. D.

Detection of Nitrogen in Organic Substances. H. Russell Ellis (*Chem. News*, 1910, **102**, 187).—The test described by Castellana (Abstr., 1905, ii, 201) is untrustworthy, owing to the fact that cyanide is formed when powdered magnesium and sodium or potassium carbonate are heated together in a limited supply of air, the nitrogen necessary to the formation of cyanide being obtained from the atmosphere. When, however, the reaction is allowed to proceed rapidly in a copious supply of air, cyanide is not formed. Similar reactions take place when mixtures consisting of magnesium and either calcium carbonate, barium carbonate, or strontium carbonate are heated in contact with a small amount of air; in these cases, cyanide, cyanamide, nitride, and carbide are formed. W. P. S.

Estimation of Ammonia Nitrogen in Water in Presence of Hydrogen Sulphide. EDWARD BARTOW and B. H. HARRISON (*J. Amer. Chem. Soc.*, 1910, **32**, 1256—1259).—The presence of hydrogen sulphide in a water interferes with the Nessler test. When a large amount of ammonia is present, the hydrogen sulphide may be removed by precipitation with a salt of zinc or lead, and the ammonia can then be estimated directly by the Nessler reagent. If, however, the quantity of ammonia is small, and it is desirable to distil and test the distillates, the results obtained are inaccurate. It has been found that accurate results can be obtained by the following method. To 500 c.c. of the water, a measured quantity of *N*-sulphuric acid is added, and 100 c.c. are distilled; by this means the hydrogen sulphide is completely removed. A volume of *N*-sodium hydroxide equal to that of the sulphuric acid used is now added, the water is again distilled until 200 c.c. have collected, and the Nessler test is applied to the distillate. E. G.

Estimation of Small Quantities of Nitrogen by Pelouze's Reaction. A. T. DAVENPORT (*J. Amer. Chem. Soc.*, 1910, **32**, 1237—1241).—A method is described for estimating small quantities of nitrogen occurring in the form of nitrates by Pelouze's reaction, which consists in the oxidation of ferrous chloride in presence of hydrochloric acid. A diagram of the apparatus is given.

The most important features of this method are the measurement of the volume of gas over sodium hydroxide solution in a jacketed burette, graduated to 1/20 c.c., as in the Schultze-Tiemann method, and the correction of the volume by comparison with a standard volume contained in another burette under exactly the same conditions. The process is simple and easily manipulated, permits of an estimation being carried out in ten minutes, and gives accurate results. E. G.

Easy Detection of Arsenic; Rapid Separation of Arsenic and Some Other Metals from Liquids. C. E. CARLSON (*Zeitsch. physiol. Chem.*, 1910, **68**, 243—262).—On adding hydrogen sulphide to an acid solution of arsenious acid, or thioacetic acid to a solution of arsenic acid, arsenious sulphide is precipitated, but if the amount is only a fraction of a mg., the separation takes a long time. If, however, ether is added, or preferably a mixture of ether and chloroform, and the whole well shaken, the ethereal layer contains all the arsenious sulphide in suspension or in pseudo-solution. Addition of alcohol promotes the separation. On being evaporated on the water-bath, arsenious sulphide is left, which may then be further identified by the mirror test. When testing urine (or other organic liquid), this is evaporated to dryness and the residue is distilled with hydrochloric acid and some ferric chloride; the distillate is diluted with solution of hydrogen sulphide and shaken with ether. The quantitative process is, briefly, as follows: The ethereal residue is heated with 1 c.c. of 30% sulphuric acid and 2 c.c. of 5% potassium permanganate for ten to fifteen minutes. The arsenic acid formed is reduced to the arsenious state by heating for half an hour at 50—70° with addition of 10 c.c. of strong solution of sulphur dioxide, and the

solution is finally evaporated nearly to dryness. Another 5 c.c. of sulphur dioxide are added, and the evaporation is repeated. The residue is now dissolved in 15 c.c. of water, 2 grams of sodium hydrogen carbonate are added, and the arsenic is titrated with $N/100$-iodine with starch as indicator.

Other sulphides, such as those of lead and mercury, are also taken up readily by ether. L. DE K.

Estimation of Potassium by the Cobaltinitrite Method. L. T. BOWSER (*J. Ind. and Eng. Chem.*, 1909, 1, 791—798).—A detailed account of the methods employed, and the results obtained by previous workers, those of Drushel and of Adie and Wood being fully discussed, and stated to be unsatisfactory in several ways when repeated by the author, who suggests the following modifications. The potash is brought into solution, any excess of acid driven off, and the residue boiled with sodium carbonate to remove any interfering metals, the filtrate concentrated, acidified with acetic acid, and the potassium precipitated with excess of the reagent according to the equation:

$$Na_6Co_2(NO_2)_{12},H_2O + 2K_2SO_4 = 2K_2NaCo(NO_2)_6 + H_2O + 2Na_2SO_4.$$

This precipitate can be boiled with sodium hydroxide, the precipitated cobalt hydroxide, $Co(OH)_2$, separated, and the filtrate and washings titrated with potassium permanganate, the reaction being:

$$10KNO_2 + 20NaNO_2 + 6K_2Mn_2O_8 + 33H_2SO_4 = 11K_2SO_4 + 10Na_2SO_4 + 12MnSO_4 + 30HNO_3 + 18H_2O;$$

or the precipitate can be treated directly with potassium permanganate, when a more complicated reaction occurs, owing to tervalent cobalt being reduced to bivalent, and thereby releasing one atom of oxygen, which oxidises some of the precipitate:

$$10[K_2NaCo(NO_2)_6,H_2O] + 11K_2Mn_2O_8 + 58H_2SO_4 = 21K_2SO_4 + 5Na_2SO_4 + 10CoSO_4 + 22MnSO_4 + 60HNO_3 + 38H_2O.$$

Likewise, the di-potassium-sodium-cobaltinitrite may be collected on asbestos, oxidised by hot standard potassium permanganate, which is decolorised by an excess of standard oxalic acid, and then titrated back with permanganate.

The influences exerted on the reaction by (1) varying the concentrations of the solutions; (2) the presence of other salts, and (3) the acid with which the potassium is combined are also investigated, and the results tabulated. F. M. G. M.

Rapid Estimation of Copper, Silver, Cadmium, and Bismuth by means of the Mercury Cathode and Stationary Anode. RAYMOND C. BENNER (*J. Amer. Chem. Soc.*, 1910, 32, 1231—1237).—Stoddard (Abstr., 1909, ii, 347) has described a method of electro-analysis by means of a mercury cathode and a stationary platinum gauze anode, in which the evolution of the gas by the current causes sufficient agitation of the liquid to enable the metals to be deposited in an adherent form. This method has now been applied to the estimation of copper, silver, cadmium, and bismuth. The apparatus is as simple as any other form of electrolytic apparatus employed for the purpose, the metal is deposited nearly as rapidly as by the rotating anode and mercury cathode, and the results are as accurate as those obtained by other methods in which mercury is used as the cathode.

The precipitation is complete in twenty minutes with copper, ten minutes with silver and cadmium, and twenty-five minutes with bismuth. E. G.

Volumetric Estimation of Mercury by means of Ammonia. G. BRESSANIN (*Boll. chim. farm.*, 1910, **49**, 589—591 *).—Archetti's method, based on the estimation of the acid liberated according to the equation $HgCl_2 + NH_3 = NH_2HgCl + HCl$, only gives quantitative results when four times the molecular quantity of ammonia is taken for the reaction, the excess being afterwards estimated by titration with litmus. R. V. S.

Estimation of Indium with the Use of a Mercury Cathode. LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, **32**, 1248—1250).—It has been found that the indium in a solution of indium sulphate containing a little free acid can be satisfactorily estimated electrolytically with the use of a rotating mercury cathode. When 10 c.c. of the solution containing about 0·10 gram of metal were used, with a current of 2—4 amperes, an *E.M.F.* of 6·5—7·5 volts, and an anode rotating 750 times per minute, the precipitation was complete in fifteen minutes. Estimations were also made by using a platinum cathode and a rotating platinum spiral anode; in presence of 0·1 c.c. of concentrated sulphuric acid and a few drops of gelatin, an adherent deposit of indium was obtained in twenty-five minutes. A potassium cyanide electrolyte and one containing Rochelle salt also proved satisfactory. E. G.

Volumetric Method for the Estimation of Manganese. FLOYD J. METZGER and ROBERT F. MCCRACKAN (*J. Amer. Chem. Soc.*, 1910, **32**, 1250—1251).—Metzger and Heidelberger (this vol., ii, 656) have stated that when a solution of manganese in sulphuric acid is treated with sodium bismuthate, it is oxidised to the quadrivalent state. A method has now been devised for estimating manganese by means of this reaction.

Fifty c.c. of a standard manganese solution are treated with 10—15 c.c. of concentrated sulphuric acid, 1—2 grams of finely-powdered sodium bismuthate are added to the cooled liquid, and the mixture is heated in a water-bath until the basic bismuth compound subsides in a granular form. The flask is cooled, a known excess of ferrous sulphate solution is added, the liquid is diluted to about 200 c.c., and titrated back with standard potassium permanganate. The value of the permanganate in terms of iron multiplied by 0·4918 gives the value in terms of manganese.

The method is rapid, and the end-point is sharp and distinct. It is being applied to the analysis of spiegel and manganese ores. E. G.

Estimation of Manganese in Potable Water. J. RODENBURG (*Chem. Weekblad*, 1910, **7**, 877—879).—As the tint of the solution of permanganate obtained in the estimation of manganese in potable water by the persulphate method usually differs from that of the colorimetric standard made from potassium permanganate, the author employs as standard one or more c.c. of a solution of manganese

* and *Ann. Chim. anal.*, 1910, **15**, 413—419.

ammonium sulphate containing 0·0025 gram Mn_3O_3 per litre, this solution being oxidised with persulphate in the same way as the sample under investigation. This difference of tint being due to chlorides in the sample, they must be eliminated. The author's procedure is as follows: 50 c.c. of the sample are boiled for several minutes with 5 c.c. of 50% nitric acid, a slight excess of silver nitrate solution added, and then 10 c.c. of a 10% solution of ammonium persulphate. The solution is brought to the boiling point, cooled, and compared with the standard tint. The method will show the presence of 0·025 mg. of Mn_3O_4.

A. J. W.

Detection of Small Quantities of Manganese in Foods. DUMITRESCOU and E. NICOLAU (*Ann. Falsif.*, 1910, 3, 370—372).—The material is incinerated, the ash is treated with nitric acid, evaporated to dryness, the residue is dissolved in water, and the solution is filtered. A portion of the filtrate is then mixed with an equal volume of a 40% ammonium persulphate solution, 1 drop of a 2% cobalt nitrate solution is added, and the mixture is heated to boiling. Should manganese be present, a pink coloration develops, due to the formation of permanganate. The authors have detected the presence of manganese in such substances as flesh, brain, bile, peas, beans, lentils, cereals, plums, eggs, milk, wine, etc., by means of this test.

W. P. S.

Error in Permanganate Titrations. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1910, 32, 1204—1207).—It has been shown by Bray and MacKay (this vol., ii, 996) that when an iodide is titrated directly with potassium permanganate, the latter is not completely reduced to the manganous state and an error results, amounting to about 0·10 c.c. of a 0·12*N*-permanganate solution. It is evident therefore that the reduction of the permanganate takes place in stages, and it is probable that a similar error may occur in other cases of titration with this salt. Skrabal (Abstr., 1908, ii, 17) has shown that the reduction from the manganic to the manganous state by oxalic acid is a slow reaction, and that a stable complex is formed between the manganic salt and the oxalic acid.

Experiments have therefore been made to ascertain the conditions in which the error due to incomplete reduction of permanganate is appreciable in oxalic acid titrations, and it has been found that the error varies from 0·01 to 0·14 c.c. of a 0·12*N*-permanganate solution, and is negligible if the acid is present in only small amount and the final temperature is 70—80°.

An investigation is being carried out with the object of determining whether there is an appreciable error in the titration of ferrous sulphate solutions with permanganate.

E. G.

The Determination of Iron and Aluminium in Inorganic Plant Constituents. R. F. HARE (*J. Ind. and Eng. Chem.*, 1910, 2, 27—28).—The estimation of iron and aluminium in the presence of manganese, calcium, magnesium, and phosphoric acid is a difficult one, and no satisfactory process has been suggested previously.

A solution of, and representing one gram of, the ash is treated with more than sufficient pure ferric chloride to combine with all the phosphoric acid; sodium carbonate is added until a permanent precipitate is just formed, which is then redissolved with 1 c.c. of 80% acetic acid, and the solution boiled for three or four minutes and rapidly filtered; the precipitate is dissolved in hydrochloric acid, and the iron and aluminium reprecipitated with ammonium hydroxide, dried, ignited, and weighed; this weight, minus the phosphoric acid and ferric oxide (found by other methods) and the ferric oxide added, will give the weight of aluminium oxide in the ash. A great deal depends on the proper adjustment of the amounts of sodium carbonate and of acetic acid added, an excess of either causing serious error. The addition of ferric chloride gives a more easily filtered and washed precipitate, and ensures complete precipitation of phosphoric acid.

The iron is determined in a fresh solution of the ash by the Zimmermann-Reinhardt method, the ferric iron being instantly reduced with stannous chloride, and titrated with potassium permanganate in the presence of hydrochloric acid after the addition of a "titrating solution" of manganese sulphate, phosphoric and sulphuric acids.

This method is claimed to be more accurate and rapid than when zinc is employed for the reduction of the ferric salt. F. M. G. M.

Estimation of Ferrous Oxide in Silicates. MAX DITTRICH and A. LEONHARD (*Ber. Vers. Oberrheinisch. Geol. Ver.*, 1910, ii, 92—93).—The process usually employed is that recommended by Pebel-Dölter, consisting in heating the silicate with a mixture of sulphuric and hydrofluoric acid in an atmosphere of carbon dioxide. The solution is then titrated with permanganate as usual.

The authors, however, state that if the silicate contains manganese also, the titration proceeds in an irregular manner, and the results become untrustworthy. This may be prevented by adding to the acid mixture 1—2 grams of potassium sulphate; the titration will then proceed normally. L. DE K.

Ammonium Perchlorate as a Reagent. Metalammine Perchlorates. ROBERTO SALVADORI (*Gazzetta*, 1910, **40**, ii, 19—21).—Perchlorates of the metallic ammines are obtained by adding a 20% solution of ammonium perchlorate in ammonia, D 0·90, to ammoniacal solutions of metallic salts. Precipitation is complete in the case of cobalt, nickel, manganese, and cadmium, even in dilute solutions. Zinc is incompletely precipitated, and copper only slowly from very concentrated solutions. The mercury precipitate is soluble in an excess of the reagent. The method may be used for the separation of cadmium from the sulphides of the second group. The sulphides are dissolved in nitric acid, excess of ammonia is added, and the bismuth is removed by filtration. The ammoniacal solution of ammonium perchlorate is added to the filtrate, and the cadmium is immediately precipitated, carrying with it a small quantity of copper.

The reagent may also be used to separate a cobalt salt from a cobalt-ammine salt. In presence of an excess of ammonium perchlorate, and out of contact with air, cobalt is completely precipitated as the compound

$Co(ClO_4)_2,6NH_3$, the cobaltammine remaining in solution (compare this vol., ii, 959).

The *cadmium* and *zinc* compounds form white crystals,

$$Cd(ClO_4)_2,4NH_3,$$

and $Zn(ClO_4)_2,4NH_3$ stable at 100°, melting at about 220°, and decomposing rapidly at 250°. They explode by percussion or if heated rapidly. C. H. D.

Detection of Small Quantities of Nickel. ALBERTO BIANCHI and ETTORE DI NOLA (*Boll. chim. farm*, 1910, **49**, 517—520).—Nickel-plating may be recognised without damage to the object by moistening it with a drop of acid, which is then absorbed by blotting paper or allowed to fall on to a porcelain surface, rendered alkaline with ammonia, acidified with acetic acid, and tested with dimethylglyoxime. In the presence of acetic acid there is no possibility that the red coloration will be masked by other coloured substances (cupric hydroxide, ferric hydroxide). R. V. S.

Estimation of Tin in Presence of Antimony. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1910, [iv], 7, 890—894).—The process depends on the fact that whilst ferric chloride is reduced quantitatively by stannous chloride, it is unaffected by antimonous chloride.

In the case of a simple mixture of the two chlorides, the solution is titrated with a standard ferric chloride solution in presence of hydrochloric acid, the formation of a permanent greenish-yellow coloration being taken as the end-point. Where both substances must be estimated, they are converted into their sulphides in the usual manner, and the mixture of sulphides treated with hydrochloric acid and potassium chlorate. To this solution aluminium is added, and when the reduction is completed, the antimony is filtered off and the filtrate and washings diluted to a known volume with diluted hydrochloric acid (50%) and titrated with a ferric chloride solution, which has been standardised against a solution of stannous chloride containing the equivalent of 1% of tin. The precipitated antimony is dissolved by means of hydrochloric acid and iodine solution, and estimated as the sulphide. 0·1 Gram of tin in presence of 1·1 gram of antimony can be estimated accurately by this method. T. A. H.

Analysis of Tin-Antimony Alloys. LEROY W. MCCAY (*J. Amer. Chem. Soc.*, 1910, **32**, 1241—1248).—It has been shown in an earlier paper (Abstr., 1909, ii, 351) that the separation of tin and antimony can be effected by taking advantage of the fact that when a dilute solution of hydrofluoric acid, containing tin in the stannic condition and antimony in the antimonious state, is treated with hydrogen sulphide, only the antimony is precipitated.

The following method is recommended for the analysis of alloys of tin and antimony. From 0·5 to 1 gram of the alloy in the form of filings or fine borings is heated rapidly with concentrated sulphuric acid in a quartz or porcelain dish until fumes of sulphuric anhydride begin to escape, and the heating is then continued for half an hour. If the liquid is now clear and the residue, consisting of lead sulphate, is

quite white, the dish is cooled and its contents are transferred to a 250 c.c. platinum dish containing 5 c.c. of hydrofluoric acid (48%) and 20 c.c. of water. The solution is heated until it boils, and is then diluted to 150 c.c., and 50 c.c of 95% alcohol are added. When the lead sulphate has subsided, it is collected, washed with water containing one-fourth of its volume of alcohol and a little sulphuric acid, and is dried, ignited, and weighed. The filtrate is collected in a large platinum dish, diluted to about 450 c.c., and treated with a rapid current of hydrogen sulphide for an hour. The precipitate is collected, washed with a saturated solution of hydrogen sulphide containing acetic acid, and afterwards digested repeatedly with colourless sodium sulphide solution. The cupric sulphide, which is left after this treatment, is dissolved in nitric acid, and the copper estimated electrolytically. The sodium sulphide solution is acidified with sulphuric acid, and the antimony precipitate is converted into the black anhydrous sulphide. The tin in the filtrate from the copper and antimony sulphides may be estimated by evaporating the liquid and subsequently heating it until sulphuric anhydride fumes are evolved, and precipitating the tin as stannic acid by pouring the sulphuric acid solution into an excess of water. E. G.

Separation of Bismuth from Alloys containing also Lead and Tin. CHARLES E. SWETT (*J. Ind. and Eng. Chem*, 1910, **2**, 28).—The following expedient is suggested as a means of overcoming the difficulties usually experienced in this estimation. The nitric acid filtrate from the stannic oxide is treated with a moderate excess of potassium or sodium hydroxide, which precipitates bismuth and cadmium, if present, and redissolves the lead hydroxide. The hydroxides are collected, washed, and redissolved in hydrochloric acid, the bismuth being then separated as oxychloride by pouring into a large quantity of water. F. M. G. M.

Rapid Methods for the Analysis of Water. ARISTIDE DANÉ (*Chem. Zeit.*, 1910, **34**, 1057—1058).—In order to ascertain whether a water is suitable for drinking, the author recommends that the following estimations be made: The calcium and magnesium present may be estimated volumetrically, the former by the titration of its oxalate, after this has been precipitated and separated in the usual way, and the latter by precipitating it as ammonium magnesium phosphate and titrating this salt with a uranium solution. Sulphates are titrated with barium chloride solution, and the total carbon dioxide is titrated with barium hydroxide-sucrose solution, allowance being made for the alkalinity of the water. Nitrites are estimated colorimetrically by means of the indole reaction, and the proportion of organic matters is estimated by heating the water with permanganate solution in the presence of sodium carbonate. The organic matters may also be estimated by titration according to Deniges' cyanide-silver nitrate method. Should further information be required as to the quality of the water, the ammonia, chlorides, nitrates, etc., may be estimated, the usual methods being employed for the purpose.

In addition, tests may be applied for the detection of *Bacterium coli.*

W. P. S.

Acid Content of Moor Water. KURD ENDELL (*J. pr. Chem.*, 1910, [ii], **82**, 414—422).—The acidity of moor water has been determined by direct titration with *N*/100-potassium hydroxide. The method of adding standard barium hydroxide and titrating the excess does not give trustworthy results, the titre decreasing with time, probably owing to the action of the alkali on humus substances present as sols. Before titration, it is necessary to dialyse the water in order to get rid of humus substances. The moor water of the red and of the black moors of the Rhone are 0·007 normal. The water of the Paulsborner moor is 0·0063 normal, the acidity being due entirely to carbonic acid.

C. S.

Estimation of Butyl and Amyl Alcohols in Alcoholic Liquids. A. LASSERRE (*Ann. Chim. anal.*, 1910, **15**, 338—341).—Instead of estimating the total quantity of higher alcohols in alcoholic liquids as is done in the Allen-Marquardt process, the method described by the author limits the estimation to that of butyl and amyl alcohols; propyl alcohol is eliminated by treating the alcoholic liquid with carbon disulphide, which extracts the butyl and amyl alcohols. After oxidation, the butyric and valeric acids are extracted from the solution by means of benzene, and their quantity estimated by titration. The details of the process are as follows: 100 c.c. of the alcoholic liquid, 70 c.c. of carbon disulphide, and 450 c.c. of saturated sodium chloride solution are placed in a separating funnel, and after the addition of a quantity of water sufficient to redissolve the precipated sodium chloride, the mixture is shaken for five minutes. The carbon disulphide is then separated, and the extraction is twice repeated, the united carbon disulphide extracts being next shaken three successive times with moderately concentrated sulphuric acid. The sulphuric acid extract is now heated to 60° in order to remove any traces of carbon disulphide, then diluted with 20 c.c. of hot water, and 5 grams of potassium dichromate and 1 c c. of concentrated sulphuric acid are added. The whole mixture is then heated in a closed flask for one hour at 50°, cooled, and diluted to a volume of 100 c.c. Twenty-five c.c. of this solution are shaken for three minutes with 30 c.c. of benzene, the latter is separated, filtered, mixed with an equal volume of alcohol, and the solution is titrated with *N*/20-alcoholic potassium hydroxide solution, using phenolphthalein as indicator. The quantity of alkali used in the titration may be calculated into amyl alcohol, but the result obtained must be multiplied by 2·082, this being the ratio of the total amount of the acids present to that portion which is obtained by one extraction with benzene. A method has been described previously (Abstr., 1907, ii, 991) for the separate estimation of butyric and valeric acids.

W. P. S.

Physico-chemical Estimation of the Ash of Wine. HENRI PELLET (*Ann. Chim. anal.*, 1910, **15**, 385).—It is pointed out that the conductivity process described by Dutoit and Duboux (this vol., ii, 552) has already been applied to the estimation of mineral matters in various substances; twenty years ago, Reichert employed the method for the estimation of ash in sugars, etc., but the results

obtained were unsatisfactory. More recently, Main, in a paper submitted to the Seventh International Congress of Applied Chemistry, London, 1909, gave the details of procedure necessary for the correct estimation of ash in sugar syrups by this process. W. P. S.

Polarimetric Estimation of Sucrose in Presence of Reducing Sugars. P. LEMELAND (*J. Pharm. Chim.*, 1910, [vii], **2**, 298—302 *).—The method is based on the observation made by Cross, Bevan, and Smith (Trans., 1898, **73**, 463) that hydrogen peroxide destroys the optical activity of reducing sugars, forming products eventually identified by Morrell and Crofts as osones (*ibid.*, 1899, **75**, 786). The author finds that lactose and dextrose are attacked by hydrogen peroxide in presence of manganese dioxide, forming optically inactive products, whilst sucrose remains unaffected. If, therefore, the optical activity of a solution containing one of these sugars and sucrose is known, the amount of sucrose can be estimated by a determination of the optical activity after the effect of the reducing sugar has been eliminated. Where a small quantity of sucrose occurs with much dextrose, the latter may be almost completely separated by treatment with alcohol of 91° (Lindet, Abstr., 1894, ii, 64), and the part soluble in alcohol may then be recovered and treated as described above.

This method is not applicable where sucrose occurs with maltose. Details of the method of working are given in the original.

T. A. H.

Detection of Inositol as a means of Identifying Wine Vinegar. P. FLEURY (*J. Pharm. Chim.*, 1910, [vii], **2**, 264—266).—A number of samples of genuine wine vinegar examined by the author all contained distinct quantities of inositol; the detection of inositol is, therefore, considered to be of use in determining the genuineness of a sample of wine vinegar. If inositol is not present, the sample is probably prepared from alcohol and not from wine. The method described previously by Meillere and Fleury (this vol., ii, 553) may be employed for detecting the inositol. W. P. S.

Estimation of Formaldehyde. WALTER BRAUTIGAM (*Pharm. Zentr.-h.*, 1910, **51**, 915—916).—The process described depends on the decomposition of formaldehyde by calcium hypochlorite; calcium carbonate is formed, and its quantity is a measure of the amount of formaldehyde present. The reaction proceeds according to the equations: $CH_2O + CaOCl_2 = HCO_2H + CaCl_2$; $HCO_2H + CaOCl_2 = CO_2 + H_2O + CaCl_2$; and $2CaOCl_2 + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2HClO$. One molecule of formaldehyde therefore yields one molecule of calcium carbonate. In carrying out the estimation, a definite volume of the formaldehyde solution is mixed in a flask with an excess of freshly prepared calcium hypochlorite solution, and the mixture is placed aside for some hours at the ordinary temperature. The clear supernatant liquid is then passed through a weighed filter, and the filtrate is heated almost to boiling in order to ascertain whether all the

* and *Ann. Chim. anal.*, 1910, **15**, 415—419.

formaldehyde has been decomposed; should such be the case, the solution remains clear, but if a further quantity of calcium carbonate forms it must be collected on the filter together with the main bulk of the precipitate. The precipitate and filter are washed until free from chlorides, dried at 100°, and weighed. W. P. S.

Estimation of Formic Acid in the Presence of Acetic Acid. H. DELEHAYE (*Ann. Falsif.*, 1910, **3**, 386—388).—The method proposed depends on the reduction of mercuric sulphate to insoluble mercurous sulphate. A quantity of the solution under examination, containing not more than 0·2 gram of formic acid, is mixed with 50 c.c. of mercuric sulphate solution (prepared as described below) and boiled under a reflux apparatus for forty-five minutes. The mixture is then cooled rapidly, the liquid is decanted through a weighed filter, and the volume of the filtrate is measured; the precipitate is then rinsed on to the filter with the aid of a saturated mercurous sulphate solution, washed with 50% alcohol, dried at 110°, and weighed. To the weight found is added a quantity in the proportion of 0·20 gram for every 100 c.c. of the filtrate; the weight thus corrected is then multiplied by 0·0927 to obtain the amount of the formic acid. The mercuric sulphate solution employed is prepared by mixing 10 grams of mercuric oxide with 20 c.c. of hot water, adding sulphuric acid until the oxide has dissolved, and diluting the mixture to a volume of 250 c.c. The filtrate obtained in the estimation should measure not less than 100 c.c., and the filtration must be carried out immediately the mixture has been cooled in order to prevent contamination of the mercurous sulphate with mercuric sulphate, which is liable to crystallise out subsequently. W. P. S.

The Separation and Estimation of Aspartic and Glutamic Acids. THOMAS B. OSBORNE and LEONARD M. LIDDLE (*Amer. J. Physiol.*, 1910, **26**, 420—425).—Aspartic and glutamic acids react acid to litmus, but their acid sodium salts do not. By Fischer's method of protein analysis, glutamic hydrochloride is usually contaminated with leucine hydrochloride, and the two cannot be separated by direct crystallisation. When, however, the solution is made neutral to litmus, leucine crystallises out readily, and from the mother liquor it is possible to separate out a further large amount of glutamic hydrochloride. It was found possible to effect a fairly satisfactory separation of leucine and aspartic acid by taking out a small fraction of the esters after most of the leucine had distilled over and before the aspartic ester begins to distil freely, and then treating this separately by a method described with detail in the text. W. D. H.

Methods for the Detection and Volumetric and Gravimetric Estimation of Salicylic Acid in Wines, and its Detection in Cases of Poisoning. GUISEPPE CATTINI (*Boll. chim. farm.*, 1910, **49**, 641—649).—For the detection of salicylic acid in wine, urine, and other coloured organic products, acidification and subsequent extraction with toluene are recommended, this solvent being preferable to ether because it does not remove colouring matter from the aqueous liquid.

Various methods which have been proposed for the estimation of salicylic acid are shown to be inaccurate. R. V. S.

Estimation of Fat in Flesh. G. Diesselhorst (*Pflüger's Archiv*, 1910, **134**, 496—500).—The fat extracted from flesh or tissue by Dormeyer's process (digestion with pepsin, extraction of the digest with ether, and weighing the ethereal extract) is very impure, and, consequently, the results yielded by the method are untrustworthy. It is shown that if the dry powder is first extracted with ether in a mill, as described by Lehmann and Völtz (Abstr., 1903, ii, 702), the fat obtained has the chemical and physical properties of beef fat. When the extracted residue of flesh is subjected to further treatment by Dormeyer's process, an additional small quantity of "fat" is obtained, which is largely contaminated with substances other than beef fat. W. P. S.

Estimation of Cocoanut Oil in Admixture with Butter Fat. Noel C. Cassal and B. Henry Gerrans (*Chem. News*, 1910, **102**, 190—191).—In the process described, the fatty acids obtained from the fat are subjected to a somewhat prolonged distillation with steam at a high temperature in order to increase the difference between the titration number of the insoluble volatile fatty acids from cocoanut oil and the titration number of the insoluble volatile fatty acids from butter fat. The process is as follows: 3 grams of the fat are saponified by heating with 10 c.c. of alcohol and 2 c.c. of 50% sodium hydroxide solution; after the alcohol has been removed by evaporation, the residual soap is dissolved in 50 c.c. of boiling water, 10 c.c. of concentrated hydrochloric acid are added, and then 50 grams of anhydrous calcium chloride. The flask is now connected with a condenser and heated by means of a calcium chloride bath, b. p. 141—146°, and when the contents of the flask begin to boil, steam is admitted and the distillation is continued until 500 c.c. of distillate have been collected. The distillate is filtered as it distils over, and the filtrate is collected in a 500 c.c. flask. At the end of the distillation, the condenser tube and the fatty acids on the filter are washed with cold water to remove hydrochloric acid and soluble fatty acids, the insoluble fatty acids are then dissolved from the condenser tube and the filter by means of hot alcohol, and the solution is titrated with *N*/10-barium hydroxide solution. In the case of cocoanut oil, the insoluble volatile fatty acids require 66 c.c. of *N*/10-alkali for neutralisation, whilst those from butter fat require 16 c.c. W. P. S.

Alkylamines as Products of the Kjeldahl Digestion. C. C. Erdmann (*J. Biol. Chem.*, 8, 41—55).—Compounds containing the groups $\equiv$NMe, $-$NHMe, or NMe_3 can yield mono-, di-, or tri-methylamine on digestion with sulphuric acid and a catalyst. The separation of organic base from ammonia in the Kjeldahl distillate is effected by adding to the neutralised solution 5—10 c.c. of an alkaline mixture containing 20% of sodium hydroxide and 30% of sodium carbonate, and 0·1 gram of yellow mercuric oxide for every c.c. of *N*/10-base present. After shaking for one hour in the dark, and keeping till the mercury

has settled, an aliquot part of the supernatant liquid is distilled. The ammonia is retained by the mercuric oxide, and the organic base which distils is titrated. The ammonia is then estimated by difference.

The author suggests that the method can be used as a general qualitative method for determining in nitrogenous substances the presence of alkylamine groups, and can probably also be used for approximately quantitative determinations as well. G. S. W.

Vortmann's Nitroprusside Reaction for Hydrogen Cyanide. H. J. VAN GIFFEN (*Pharm. Weekblad*, 1910, **47**, 1043).—A modification of Vortmann's process for the detection of hydrogen cyanide. Although not quite so delicate as the original method, it has the advantage of not being interfered with by the presence of alcohol.

To a portion of the distillate are added a few pieces of sodium nitrite and then 2 or 3 drops of officinal ferric chloride solution. To the brownish-yellow liquid is then added dilute sulphuric acid drop by drop, when effervescence takes place and the liquid turns bright yellow. After heating to boiling, the iron is precipitated by adding excess of ammonia, and the filtrate is evaporated to dryness on the water-bath. The residue is dissolved in a little water, and the solution cooled in ice. On adding a drop of dilute ammonium sulphide, a violet colour is formed, which, according to the amount of cyanide present, more or less rapidly passes into blue, green, and yellow. L. DE K.

Estimation of Nitrogen Existing as Cyanamide and as Dicyanodiamide in Calcium Cyanamide. ALBERT STUTZER and J. SÖLL (*Zeitsch. angew. Chem.*, 1910, **23**, 1873—1874).—An extract of calcium cyanamide is first prepared by shaking the substance (10 grams) with 400—450 c.c. of water for two and a-half hours in a rotary apparatus. The flask is then filled to the mark (500 c.c.) and the contents filtered.

The nitrogen in the form of cyanamide is estimated in 25 c.c. (=0·5 gram of substance) by adding 10 c.c. of silver acetate solution (prepared by adding 400 c.c. of 10% ammonia to 100 grams of silver acetate and diluting to 1 litre). The precipitate is collected on a nitrogen-free filter, and after all the solution has run through and the beaker below the filter has been changed, is washed with water, and the nitrogen determined by the Kjeldahl method.

The nitrogen as dicyanodiamide is estimated in the undiluted filtrate from silver cyanamide (25 c.c. =0·357 gram of original substance) by adding 10 c.c. of 10% potassium hydroxide solution, and estimating the nitrogen in the precipitated silver dicyanodiamide.

In directly estimating the dicyanodiamide, an alcoholic extract is made by shaking the substance (10 grams) for an hour with 250 c.c. of 94% alcohol. A portion of the filtered extract (100 c.c.) is evaporated to dryness, dissolved in hot water, treated with 10 c.c. of the silver acetate solution, filtered, and the precipitate washed. The filtrate is then mixed with 10 c.c. of 10% potassium hydroxide, at once filtered, and then estimated by Kjeldahl's method.

N. H. J. M.

Calcium Cyanamide; its Analysis and the Changes in Composition it Undergoes when Exposed to the Atmosphere. CH. BRIOUX (*Ann. Chim. anal.*, 1910, **15**, 341—346).—Calcium cyanamide gradually undergoes decomposition when exposed to moist air, the calcium being converted into calcium hydroxide and carbonate, and cyanamide is liberated; the latter polymerises to form a double molecule, dicyanodiamide. All these changes proceed more rapidly when the air contains carbon dioxide and is saturated with moisture; under these conditions, as much as 80% of the soluble nitrogenous compounds present in calcium cyanamide may be converted into dicyanodiamide in the course of a few months. As dicyanodiamide has toxic properties and is injurious to vegetation, it is of some importance to know to what extent the decomposition has proceeded in any sample of calcium cyanamide which has been stored in sacks or bags. This may be ascertained by estimating the cyanamide and dicyanodiamide present in a solution of the calcium cyanamide, and the process recommended for the purpose depends on the fact that cyanamide yields a precipitate with silver nitrate which is insoluble in excess of ammonia, whilst the analogous precipitate obtained in the case of dicyanodiamide is soluble in ammonia; further, both substances are precipitated by silver nitrate in the presence of potassium hydroxide. One gram of the calcium cyanamide is shaken with 250 c.c. of water for three hours, and the solution is then filtered; 100 c.c. of the filtrate are now treated with 20 c.c. of 5% silver nitrate solution, and an excess of ammonia is added. The precipitate is collected on a filter, washed first with dilute ammonia, then with water, and is next dissolved in warm dilute nitric acid (a small quantity of black residue sometimes remains insoluble), and the amount of silver thus obtained in solution is titrated with *N*/10-ammonium thiocyanate solution; each c.c. of the latter solution is equivalent to 0·0014 gram of nitrogen. A second quantity of 100 c.c. of the filtrate is then treated with silver nitrate solution in the presence of an excess of potassium hydroxide; the precipitate formed is collected, and the nitrogen in it is estimated by Kjeldahl's method. The difference between the amounts of nitrogen found in the two estimations gives the nitrogen present in the form of dicyanodiamide. W. P. S.

Estimation of Digitoxin in Foxglove Leaves and their Preparations. JAMES BURMANN (*Bull. Soc. chim.*, 1910, [iv], 7, 973—982).—It is now known that the three chief glucosides of foxglove leaves are digitoxin, digitalin, and digitonin, of which the first is of primary physiological importance and is the one usually estimated for medical purposes. Keller's method of estimation (Abstr., 1898, ii, 267, 657) is that generally used, and a comparison has therefore been made between the amorphous digitoxin (ψ-digitoxin) isolated by this method of estimation and (*a*) crystalline digitoxin and (*b*) Cloetta's soluble digitoxin (digalene of commerce).

The results show that ψ-digitoxin and Cloetta's soluble digitoxin are both amorphous and are practically identical in melting point, solubility, and physiological activity, and that both are less active than crystalline digitoxin and show quite different physical constants.

Keller's process can only be regarded as useful in estimating the medicinal value of the drug and its preparations if it is admitted that in the product weighed there is a constant relation between the digitoxin and the other glucosides present. T. A. H.

Estimation of Adrenaline in Normal Blood and after its Injection by means of Physiological Methods. Paul Trendelenburg (*Arch. expt. Path. Pharm.*, 1910, 63, 171—176).—See this vol., ii, 971.

Estimation of Caffeine in Roasted Coffee. C. Virchow (*Chem. Zeit.*, 1910, 34, 1037—1038).—Twenty grams of ground coffee are moistened with about 10 c.c. of water, and the mass is introduced into a shaking cylinder furnished with a stopcock and ground stopper. One hundred c.c. of chloroform are added, and the whole is well shaken for a minute. The chloroform is drawn off, and the extraction is repeated twice. To the united filtrate is added 1 gram of paraffin, and the chloroform is recovered by distillation. To the residue in the flask are then added 25 c.c. of hot water, the liquid is poured into a beaker, and the flask rinsed twice with 25 c.c. of hot water. The mixture is well stirred, then allowed to cool, and filtered; no caffeine is retained by the paraffin. On evaporating the aqueous solution, crude caffeine is left, which may be weighed. It is then purified by redissolving it in water, and again evaporating to dryness with addition of a little magnesium oxide and extracting the mass thrice with chloroform; on evaporating this, almost pure caffeine is left, but it is advisable by way of a check to ascertain its nitrogen content by means of a Kjeldahl estimation. L. de K.

Toxicological Detection of Colchicine. Hermann Fühner (*Arch. exp. Path. Pharm.*, 1910, 63, 357—373).—Colchicine can in forensic cases be detected with certainty by a combination of chemical and biological tests. A slight modification is proposed in Zeisel's test. 0·1 mg. kills a white mouse. In frogs the toxicity of colchicine is increased 500-fold by warming them to 30—32°, and immunity can be produced in the usual way. In frogs, if the drug is introduced under the skin, it in part re-appears in the urine. W. D. H.

Estimation of "Saccharin" in Urine. W. R. Bloor (*J. Biol. Chem.*, 1910, 8, 227—232).—Methods previously proposed for the estimation of "saccharin" in the urine after its administration are not sufficiently exact when dealing with small quantities. The new method proposed is colorimetric and gives good results; the colour is due to the transformation of "saccharin" into what is probably phenolsulphonephthalein (sulphurein) by treatment with a phenolsulphuric acid mixture, and is a bright yellow in weakly acid solutions, and purple-red in alkali. The purple fades after a time, but the yellow remains unchanged for a month or more. The test is performed with a benzene extract of the urine. W. D. H.

Estimation of "Saccharin" in Urine and Fæces. Alfred J. Wakeman (*J. Biol. Chem.*, 1910, 8, 233—236).—The method is

practically the same as Bloor's (see preceding abstract), but differs in the apparatus used, in the employment of ethyl acetate instead of benzene as solvent, and in one or two other minor points. W. D. H.

Amylases. I. Examination of Methods for Determination of Diastatic Power. HENRY C. SHERMAN, E. C. KENDALL, and E. D. CLARK (*J. Amer. Chem. Soc.*, 1910, **32**, 1073—1086).—A critical study of some of the methods in use for measuring diastatic power, carried out mainly on taka-diastase and pancreatin. The Lintner method is said to be insufficiently accurate for preparations of high diastatic power. A modified form of the iodine method is described, by means of which satisfactory results were obtained with taka-diastase, but not with pancreatin. Methods depending on the action of the latter enzyme on pure starch in pure water were found to be useless, because such a medium is too poor in electrolytes for the diastase to function normally. The optimum conditions necessary for the amylase to behave normally have been worked out and incorporated in a new gravimetric, copper-reduction method, which is described in detail. With commercial pancreatin this process gave results twenty times as high as when no electrolyte had been added. W. O. W.

Reaction Distinguishing between the Organic Derivatives of Arsenious Acid and Those of Arsenic Acid. ERCOLE COVELLI (*Boll. chim. farm.*, 1910, **49**, 50—51. Compare Abstr., 1909, ii, 830). —The difference in stability towards reducing agents in alkaline solution which is shown by the above acids is shared by their organic derivatives. Atoxyl is reduced by nascent hydrogen in acid solution, giving a yellow precipitate, whilst in alkaline solution it is not attacked. The corresponding arsenious *derivative*, $NH_2\cdot C_6H_4\cdot AsO,2H_2O$, m. p. 90°, is prepared by treating atoxyl with sulphur dioxide in the cold, and precipitating with sodium carbonate. It is reduced by nascent hydrogen in alkaline solution (aluminium and potassium hydroxide), giving a yellowish-white precipitate, and also in acid solution, with formation of a sulphur-yellow precipitate. Methylarsinic acid, which is reducible in acid, but not in alkaline solution, yields when treated with sulphur dioxide a liquid which, when reduced with potassium hydroxide and aluminium, gives a yellow precipitate and blackens a test-paper impregnated with ammoniacal silver nitrate. R. V. S.

Characteristic Reactions of Atoxyl. QUINTO FIORI (*Boll. chim. farm.*, 1910, **49**, 98—99).—Atoxyl yields an orange-red coloration with a solution of bleaching powder in the cold. Sodium methylarsinate and sodium cacodylate do not give this reaction, whilst antifebrin gives an olive-green coloration only when warmed. Mercuric chloride produces in solutions of atoxyl a white precipitate, which is soluble in dilute hydrochloric acid and in ammonia. Sodium methylarsinate gives with the same reagent a brick-red precipitate, which is also soluble in hydrochloric acid or ammonia, whilst acetaldehyde and the cacodylate yield no precipitate. The presence of arsenic in atoxyl can be shown readily after a preliminary fusion with sodium hydroxide.
R. V. S.

General and Physical Chemistry.

Influence of Temperature on the Refractive Index of White of Egg. Amedeo Herlitzka (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 251—256).—Previous observations relating to the influence of salts on the refractive index of egg-albumin are referred to. Contrary to the conclusions drawn by Frei (this vol., ii, 365), the author's data indicate that dissolved salts have no influence on the refractive index of colloids.

New measurements of the refractive indices of a series of solutions of egg-albumin have been made at temperatures between 7° and 47°. Whereas Frei's data led him to conclude that the refractive index of colloids varies with the temperature according to a linear equation, the author finds that a quadratic equation of the form $N_t = N_0(1 - K_1t - K_2t^2)$ is necessary for the representation of the temperature influence. H. M. D.

Anomalous Dispersion of Light in an Aqueous Solution of Neodymium Nitrate. L. Isakoff (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 236—243 [Physical Part]).—Some preliminary experiments on the dispersion of neodymium nitrate by the interference method. A figure of the apparatus and a table and curves of the results obtained are given. The experimental results agree well with those calculated from the dispersion formula deduced. Z. K.

Distribution of Chemical Elements in the Earth's Crust. Wladimir J. Vernadsky (*Bull. Acad. Sci. St. Petersburg*, 1910, [vi], 1129—1148).—The spectra of a large number of minerals have been investigated in the oxygen gas flame, and the results are given in a series of tables showing which elements are present, numerous notes being added regarding the origin, nature, and so forth of the minerals and elements dealt with.

Indium, thallium, rubidium, cæsium, gallium, and boron have been found for the first time in several minerals. In some natural glasses, bismuth, copper, and lead have been identified.

When the spectrum of indium is obtained by sparking a solution of a salt or a mineral containing the metal, the platinum wire continues to give the indium spectrum even after being repeatedly washed; the same phenomenon occurs with lithium; in the latter case it sometimes happens that a platinum wire which has ceased giving the lithium spectrum when dipped in pure water or acid, suddenly re-commences to give the spectrum; this may possibly be due to the formation of some compound of lithium and platinum. Various methods of determining the spectra of elements are discussed.

Z. K.

Ultra-red Line Spectra. III. Accurate Measurement of Wave-lengths greater than 27,000 Å.-U. FRIEDRICH PASCHEN (*Ann. Physik*, 1910, [iv], **33**, 717—738. Compare Abstr., 1909, ii, 630).—The experimental arrangement is described by means of which measurements of the wave-lengths of lines in the ultra-red spectra of lithium, sodium, potassium, rubidium, cæsium, and thallium have been made. Observations relating to the ultra-red spectra of cadmium, aluminium, silver, helium, and mercury are also recorded. A special form of iron-constantan thermo-element suitable for use in such measurements is described. H. M. D.

Ultra-red Line Spectra. (Spectra of Silver, Copper, Cæsium, Rubidium, Strontium, Barium.) H. M. RANDALL (*Ann. Physik*, 1910, [iv], **33**, 739—746. Compare preceding abstract).—Wave-length measurements in the ultra-red spectra between 8000 and 30,000 Å.-U. are recorded. The grating spectro-bolometer designed by Paschen was employed. H. M. D.

Relative Duration of Spectral Rays Emitted by Magnesium Vapour in the Electric Spark. GUSTAVE A. HEMSALECH (*Compt. rend.*, 1910, **151**, 668—671).—Kayser and Runge's triplets in the magnesium spectrum, as well as Rydberg's series of nebular lines, have been studied by the method previously described (*Compt. rend.*, 1905, **141**, 1227; 1910, **150**, 1743). The relative intensity of the lines is given in tabular form, together with their relative duration at two capacities. The lines of the nebular series are the more sensitive to changes in capacity. The presence of impurities in the magnesium electrodes was rendered evident by the abnormal duration of the foreign lines. The method may be of value in detecting unknown impurities in analysis. W. O. W.

Spectra of Anode Rays. OTTO REICHENHEIM (*Ann. Physik*, 1910, [iv], **33**, 747—762).—Spectral observations have been made of the anode rays which are emitted by salts of the alkali and alkaline-earth metals. In the case of the alkali metals the spectra show lines of the principal and first subsidiary series, but no lines belonging to the second subsidiary series could be detected, even on the plates which were obtained with the longest possible exposure. In general, the anode ray spectra resemble the arc spectra so far as the relative intensity of the individual lines is concerned.

The anode ray spectra of the alkaline-earth elements are much simpler than the corresponding arc spectra. The spectra of all three metals are of the same type, and consist of a series of pairs of lines having the same difference in frequency, and, further, of a single line which bears no obvious relationship to the other lines. The isolated lines in the case of calcium and strontium are the flame spectrum lines, $\lambda = 4227$ and $\lambda = 4608$ respectively. On the other hand, the isolated line found in the case of barium is $\lambda = 6142$, whereas the flame spectrum line is $\lambda = 5536$.

The lines in the anode ray spectra were found to exhibit the Doppler effect, and the magnitude of this was measured in several cases. The various observations are discussed with reference to the

question of what are the carriers of the negative electrons which are responsible for the line spectra. The author considers that the carriers in the case of both the principal and subsidiary series of lines are positively charged ions in accordance with Stark's theory.

H. M. D.

Absorption and Inversion Phenomena in Luminous Hydrogen. AL. PFLÜGER (*Ber. Deut. physikal. Ges.*, 1910, **12**, 719—724).—Polemical against Ladenburg (this vol., ii, 811). The results of the author's previous work are summarised. H. M. D.

Absorption Spectra of Sulphur Vapour at Different Temperatures and Pressures, and their Relation to the Molecular Complexity of this Element. J. IVON GRAHAM (*Proc. Roy. Soc.*, 1910, *A*, **84**, 311—324).—The absorption spectra of sulphur vapour have been photographed at temperatures varying from 530° to 900°, and at pressures ranging from atmospheric down to 10 mm. of mercury. The records obtained at constant pressure over the above interval of temperature show that two distinct absorption spectra are present, and these are attributed to the molecular complexes S_8 and S_2. The various photographs obtained at constant temperature and different pressures indicate that above 580° the S_8 molecules dissociate directly into the diatomic molecules, whereas at or below 520° dissociation takes plcae with the formation of molecules which are intermediate in complexity. The wave-lengths and frequencies of the bands which are due to the S_8 and S_2 molecules are tabulated.

The conclusions thus arrived at on the basis of spectroscopic evidence are in agreement with the views expressed by Preuner in explanation of the course of dissociation of sulphur vapour at 448°. H. M. D.

Absorption Spectra and Constitution of Benzene Derivatives. I. NICOLAI A. WALIASCHKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 751—805).—Curves and tables are given of measurements made of the absorption spectra of *o*-, *p*-, and *m*-hydroxy-, methoxy- and -acetoxy-benzaldehydes, phenol, and benzaldehyde in aqueous and alcoholic solutions of various concentrations, and with and without the addition of hydrochloric acid; also for the sodium bisulphite derivatives of benzaldehyde, for anisole, acetoxyphenol, resorcinol monomethyl ether, guaiacol in alcoholic or aqueous solution, mixtures of benzaldehyde and some of its derivatives with chloroform, and for various mixtures of benzaldehyde and guaiacol in alcoholic solution. The results are discussed in detail.

All the ortho- and meta-derivatives give absorption spectra curves of the same type as benzaldehyde, the only difference between the various spectra being that some of the bands in some compounds are more developed than in others. The meta-spectra are intermediate between those of benzaldehyde and the corresponding ortho-compound, and are more readily changed by the addition of hydrochloric acid to the alcoholic solution, the effect being to make the spectra approach nearer to that of phenol. The reason for this is the formation of the unstable compound, $OH{\cdot}C_6H_4{\cdot}CHCl{\cdot}OH$, which becomes hydrolysed on greater dilution. In water, this compound is

completely hydrolysed, consequently the addition of hydrochloric acid to an aqueous solution of the compounds has no effect. On the other hand, the ortho-benzaldehyde derivatives in aqueous solution are similarly affected by the addition of sodium hydrogen sulphite, and the greater the concentration of the latter, the more do their spectra approach that of phenol.

The *p*-hydroxy- and -methoxy-derivatives in acid and neutral alcoholic or aqueous and in chloroform solution give curves of the same type as phenol, but the spectra of the *p*-acetoxy-derivative is more like that of *o*-hydroxybenzaldehyde.

The introduction of the benzaldehyde group into the benzene ring induces a definite new state of the latter, and this effect is strengthened by the introduction in the ortho- or meta-position of an acetoxy-, methoxy- or hydroxy-group; these groups are, therefore, regarded as auxo- or batho-chromes, the influence of which on the spectra is to move the absorption bands from the violet towards the red end of the spectrum. A similar effect is produced by the acetylation of benzaldehyde in the para-position, the effect being the same as the acetylation of phenol, which greatly decreases the influence of the hydroxyl group on the benzene ring, but the hydroxy- or methoxy-group in the para-position decreases greatly the influence of the aldehyde group on the benzene ring, but has no influence on the hydroxyl group in phenol, consequently the spectra differs little from that of the latter. The absorption spectrum of a mixture of benzaldehyde and phenol in equimolecular proportions is very much like that of *p*-acetoxybenzaldehyde. A study of the complex curves obtained by mixtures of substances leads the author to reject Baly and Collie's explanation (Trans., 1905, **87**, 1332) of the benzaldehyde spectrum. On the contrary it is maintained that benzaldehyde has a greater selective absorption than phenol, and that the entrance of the aldehyde group does not retard the internal motion of the benzene, but induces a new form of vibration. The general results and conclusions drawn from the study of complex absorption spectra agree with those of Hartley (Trans., 1909, **95**, 52). Z. K.

Progressive Phosphorescence at a Low Temperature. JOSEPH DE KOWALSKI (*Compt. rend.*, 1910, **151**, 810—812).—The fluorescence of some aromatic compounds in alcoholic solution has been examined at different temperatures between $-100°$ and $-190°$. At about $-135°$ the solutions were viscous, the fluorescence extended towards the red, and was apparent even when not visible at the ordinary temperature. In the case of phenanthrene, anthracene, and others, the fluorescence terminated in the ultra-red. Fluorescence was observed below $-135°$, when the solutions solidified, whilst at $-150°$ to $-165°$ phosphorescence also appeared, the duration of the latter increasing as the temperature was lowered. A progressive phosphorescence was also observed, having an emission spectrum characteristic for the substance in solution, but independent of the temperature. The bands of which it was composed were more intense and persistent than the broad bands due to ordinary phosphorescence, which disappears as soon as the light exciting it is removed.

For each substance there was a definite temperature above which progressive phosphorescence did not appear. This temperature limit appears to be independent of the freezing point or electrical conductivity of the solution. Phenanthrene does not show the phenomenon above $-158°$. W. O. W.

Rotation Dispersion. II. HERMANN GROSSMANN and BERNHARD LANDAU (*Zeitsch. physikal. Chem.*, 1910, **75**, 129—218. Compare Abstr., 1909, ii, 713; this vol., ii, 563).—The optical rotation of methyl *l*-malate in over ninety solvents in different dilutions has been measured at 20° for red, yellow, green, light blue, dark blue, and violet light by the method already described (*loc. cit.*), and a number of measurements have also been made with ethyl *d*-tartrate. Methyl malate is specially advantageous for such measurements, owing to the fact that the dispersion curve of the pure liquid is normal, as the following figures show:

Light.	Red.	Yellow.	Green.	Light blue.	Dark blue.	Violet.
$[\alpha]^{20°}$	$-5{\cdot}62$	$-6{\cdot}42$	$-7{\cdot}57$	$-8{\cdot}96$	$-9{\cdot}49$	$-9{\cdot}86$

The dispersion curve of methyl tartrate is abnormal. For full details as to the magnitude and sign of the rotation in the different solvents in varying dilutions, the original paper must be consulted.

The more important general conclusions with reference to the action on methyl malate are as follows. In organic solvents containing halogens (over thirty such solvents were used) there is a tendency to reverse the direction of the rotation. This tendency attains its maximum when there are four chlorine atoms in the molecule; it is less when five chlorine atoms are present. Bromal, chloral, and acetyl chloride have an effect different from that of the other halogen compounds, which is accounted for by the fact that the solutions show mutarotation. Further, in most cases the rotation attains a maximum in these solvents and then diminishes somewhat, and the final value is attained only after four or five days. Somewhat similar results are obtained with ethyl tartrate. Heat is developed when the esters are dissolved in the above three solvents, so that the mutarotation is doubtless connected with chemical combination, but this does not account for the maxima.

The effect of solvents containing a hydroxyl (including carboxyl) or nitro-group is similar to those containing halogens, but solvents containing a free amino-group or a nitrogen in the ring of a heterocyclic compound markedly increase the lævorotation of the ester. That the effect just described is due to these groups is supported by the observation that when the hydroxyl or amino-group is modified by putting in alkyl or other groups, the influence on the rotation is lessened or non-existent. The methyl group, as shown by observations with hydrocarbons and fatty acids, also has a tendency to reverse the sign of the rotation. Solutions in formic acid showed mutarotation, and detailed observations on this phenomenon were made. In contrast to other groups, the aldehyde group in aliphatic compounds markedly increases the lævorotation of the ester. The same group in aromatic compounds has a similar but less pronounced influence.

As regards isomeric compounds, examples are given where a group in the meta-position has a greater influence on the rotation than when in the ortho-position. The difference in the effect of a group when in the nucleus and side-chain was analogous in all cases; the effect is greater in the latter position.

As inorganic solvents, water, sulphuric acid, arsenic trichloride, phosphorus trichloride, and phosphoryl chloride were used, and measurements with both active esters were made. Water has very little effect on the specific rotation of methyl malate. The two halogen compounds of phosphorus cause rotation to the left with both esters. Methyl malate shows mutarotation in phosphoryl chloride, but ethyl tartrate does not. Of all the solvents examined, arsenic trichloride has the greatest effect in reversing the rotation. In the violet, the specific rotation of ethyl tartrate is $-39{\cdot}64$, of methyl malate $+29{\cdot}68$. In sulphuric acid the natural rotation of the esters is considerably increased.

The observations show that anomalous rotation dispersion is by no means a rare phenomenon; it occurs in each case where the solvent has a tendency to reverse the direction of rotation of the solute.

The influence of concentration on rotation is also discussed. G. S.

Measurement of the Rotation Dispersion of Optically Active Compounds by means of the Nernst Light. HERMANN GROSSMANN and BERNHARD LANDAU (*Zeitsch. Ver. deut. Zuckerind,* 1910, 1109—1117).—The use of a Nernst lamp in combination with suitable light filters is recommended for the measurement of rotation dispersion. The rotation produced by a 1-millimetre quartz plate has been determined for the approximately monochromatic light which is obtained by use of the coloured solutions suggested as filters by Landolt and by Winther. The specific rotations of dimethyl *l*-malate and diethyl *d*-tartrate for the various coloured rays are recorded, and diagrams are given showing the influence of the solvent on the rotation dispersion of these substances in solution (see preceding abstract). H. M. D.

Liquids with Conical Focal Lines. GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.,* 1910, **151**, 762—765. Compare this vol., ii, 809).—A geometrical description and discussion of the appearances presented by anisotropic liquids of the type of ethyl azoxybenzoate when these are viewed between crossed nicols under the microscope.

W. O. W.

Triboluminescence. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci St. Petersburg,* 1910, [vi], 1037—1041).—The property of triboluminescence of substances is closely associated with their electric properties; thus where triboluminescence occurs in substances having a centre of symmetry, pyroelectric and other electric properties also occur. Triboluminescence is a surface phenomenon, and temporary triboluminescence is due to the change in the physical properties of the surface of the crystal. Z. K.

The Nature of Triboluminescence. IWAN VON OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 591—606. Compare preceding abstract).—A large number of substances, chiefly organic compounds, investigated by the author and others are tabulated with respect to their triboluminescence, and the following conclusions are drawn. If one member of a group of chemical compounds which form solid solutions with one another, or with some common substance, is permanently triboluminescent, then all the other members will be permanently triboluminescent.

An apparent exception occurs in a group of substances forming solid solutions with dibenzyl, but the latter is shown to occur in two modifications, of which the β-modification and the substances forming solutions with it are not luminescent. A permanently triboluminescent crystal does not give solid solutions with non-luminescent substances, and if one component of a solid solution is triboluminescent, then the solution is likewise triboluminescent.

The triboluminescence of a substance depends only on the system and structure of its crystals; it depends on its chemical constitution only so far as the latter influences crystalline form. Racemic mixtures of triboluminescent substances are always non-luminescent; apparent exceptions are probably not racemates, but only physical mixtures of the two compounds, or they may be cases of temporary luminescence; on the other hand, optically inactive compounds of such type as mesotartaric acid may be triboluminescent.

Only substances the crystals of which have no centre of symmetry can possess the property of permanent triboluminescence. Exceptions to this rulè observed by Vernadsky and others are either cases of temporary luminescence (for in some cases the decay of this property may take a very long time), or the crystalline form of the substance in question has not yet been accurately determined. Thus at 130°, potassium nitrate, which at that temperature exists as hexagonal crystals of the rhombohedral class, is permanently triboluminescent, but at the ordinary temperature, when the crystals belong to the rhombic system of the holohedral class, they are only triboluminescent when freshly prepared. There is also reason to think that the intensity of triboluminescence depends on the system and class to which the crystals of a substance belong. Z. K.

Triboluminescence of Racemic Compounds. IWAN VON OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 607—609. Compare preceding abstract).—The fact that racemic compounds are never triboluminescent can be used as a very rapid, simple method of distinguishing between the racemate and the mere mixture of two optically active compounds, and also to ascertain the exact point at which a racemate is resolved into its constituents and vice versa. This method may also be employed to determine exactly when one non-triboluminescent modification of a substance passes into a new crystalline, triboluminescent modification. Z. K.

Triboluminescence of Minerals. B. A. LINDENER (*Bull. Acad. Sci. St. Petersburg*, 1910, [vi], 999—1022).—A historical résumé of

the previous work done on the subject. The triboluminescence of various natural minerals has been examined, and the minerals are classified with respect to this property and their chemical constitution. The following conclusions are drawn: (1) Triboluminescence in organic substances is of frequent occurrence. (2) Whereas the triboluminescence of artificial crystals is sometimes only temporary, that of the natural crystals is constant, and does not depend on the time. (3) Minerals belonging to the most varied chemical classes and groups can show the property, but with few exceptions either all or none of the members of an isomorphous series are triboluminescent. (4) The hardness of a mineral exercises no influence, but the more brittle and the more marked the cleavage the more intense is the luminescence. (5) All triboluminescent minerals are non-conductors of electricity, and all those that have pyroelectric properties are also triboluminescent. The character of the luminescent sparks is the same for all minerals. (6) The triboluminescence does not depend on the character and temperature of the medium surrounding the mineral. After reviewing the various theories advanced to explain triboluminescence, the author draws the conclusion that the most applicable is Vernadsky's (*Bull. Acad. Sci. St. Petersburg*, 1906, 49), namely, that the triboluminescence of chemical compounds is closely dependent on their crystalline form. So far as is at present known, the crystalline form of nearly all triboluminescent substances belongs to the class in which there is no centre of symmetry. Z. K.

Oxidation of Hydrogen Iodide under the Influence of Light. B. S. Schwezoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 219 [Physical Part]).—The purpose of the research was the construction of a chemical photometer. The oxidising action of sulphuric, hydrochloric, and nitric acid on potassium iodide in diffused sunlight was investigated in a special apparatus, of which a figure is given. A constant current of air passing through the mixture kept the concentration of oxygen in it constant. Nitric acid reacts rapidly even in the dark; sulphuric and hydrochloric acid react much more slowly, and with about the same velocity. The order of reaction, calculated by the formula

$$n = (\log Q - \log Q_2)/(\log C_1 - \log C_2)$$

(Q and Q_2 = concentration of the separated iodine; C_1 and C_2 the concentration of potassium iodide) is 2 for dilute solution, and 2·25 for concentrated solutions (compare Plotkinoff, Abstr., 1907, ii, 212; 1908, ii, 790). Equivalent quantities of sodium, potassium, and cadmium iodide under similar conditions evolve equal quantities of iodine. Z. K.

Chemical Changes Produced by Different Kinds of Rays. IV. Catalytic Action of Sunlight in the Presence of Inorganic Substances. Carl Neuberg (*Biochem. Zeitsch.*, 1910, **29**, 279—293. Compare Abstr., 1908, ii, 915).—The author summarises the chemical changes already investigated when various substances are exposed to sunlight in the presence of uranium salts. He now shows that various other inorganic substances exert a similar action, and gives the qualitative results of the exposure of solutions of forty-five different substances in the presence of ferric sulphate. Most of these substances show changes of degradation. Certain reactions were also

quantitatively investigated. In the case of alcohols, the amount of aldehyde formed was estimated; in that of α-amino-acids and peptones, the amount of ammonia evolved in deamidisation; in that of β-amino-acids, the amount of amino-aldehyde formed. In the case of *l*-glucose, the diminution of fermentable sugar was estimated, and in those of the disaccharides, the amount of inversion. The amount of uric acid destroyed was also estimated, and also the amount of phosphoric acid set free from nucleic acids, and the amount of salicylic acid formed from benzoic acid. S. B. S.

Photo-electric Experiments with Anthracene. WALTER STEUBING (*Ber. Deut. physikal. Ges.*, 1910, **12**, 867—868).—A reply to criticism on the part of Byk and Borck (this vol., ii, 814) of previous experiments by Stark and Steubing (Abstr., 1908, ii, 746) on the photo-electric sensitiveness of anthracene. The experimental arrangement employed is described, and reasons are advanced in support of the validity of the conclusion that anthracene is photo-electrically active. H. M. D.

Nature of the Ionisation Produced by α-Rays. FRANK E. WHEELOCK (*Amer. J. Sci.*, 1910, [iv], **30**, 233—255).—Experiments have been made to test whether columnar ionisation affords a complete explanation of the lack of saturation obtained in α-ray ionisation when moderate fields are employed, or whether "initial re-combination" also plays any part. With a perpendicular field, the lack of saturation is less than with a parallel field, as Moulin found (Abstr., 1908, ii, 921). The ratio of two currents obtained with a constant field and two sources of α-rays differing in intensity does not depend on the field when it is parallel to the path of the rays, but does when it is perpendicular, as though with strong currents the ions in different columns interspersed with one another. A theoretical expression based on the hypothesis of columnar ionisation gave a saturation curve different from the experimental, saturation being approached, as the field increases, more slowly than the expression required. On this and other data, the conclusion is drawn that possibly both the hypotheses of columnar ionisation and of initial re-combination may be necessary to explain all the peculiarities of α-ray ionisation. F. S.

Absorption and Reflexion of the β-Particles by Matter. ALOIS F. KOVARIK (*Phil. Mag.*, 1910, [vi], **20**, 849—866).—The radioactive substances employed, radium-*D* and -*E*, actinium-*C*, radium-*B*, thorium-*A*, -*B*, -*C*, and -*D*, were deposited on very thin aluminium leaf the absorption and scattering of which is negligible. Such preparations covered directly with thin aluminium foil and placed some distance below the electroscope, give an absorption curve showing an increase in the ionisation for the first 0·05 to 0·01 mm. of aluminium, or equivalent thickness of tin, which is ascribed to scattering. When the distance of the absorbing foils from the preparation was increased, the maximum decreased in magnitude, until finally the reverse effect, studied by Crowther, showed itself. In a hemispherical ionisation chamber, arranged so that the path of all rays was the same, it was shown that

the rays reflected from the support beneath the preparation were always less penetrating than the direct rays, the less so the greater the atomic weight of the reflector. Measurements of the absorption coefficients of the various rays were taken with as much aluminium below as above the preparation to compensate for reflexion. The curves obtained were very nearly exponential.

For different β-rays the percentage of the radiation reflected increases with increase in the velocity of the rays and with the atomic weight of the reflector. For very penetrating β-rays [$\lambda(\text{cm.})^{-1}$ above 20], however, the percentage reflected again decreases. By multiple reflection from the sides of the ionisation chamber, the ionisation may be increased three and a-half times. F. S.

The Reflexion of Homogeneous β-Particles of Different Velocities. ALOIS F. KOVARIK and W. WILSON (*Phil. Mag.*, 1910, [vi], 20, 866—870).—The β-rays of radium *C*, from a sealed bulb of radium emanation, were sorted out into homogeneous rays by a magnetic field, and entered a flat ionisation chamber, made of thin aluminium leaves, which could be inclined at different angles to the rays, and could be covered with reflecting substances. It was found that the power of substances to reflect the rays increased with the velocity of the rays, from $H\rho = 1000$ to $H\rho =$ about 3000, and then slightly decreased again, but the ratio of the reflective powers of lead and copper was the same whatever the velocity of the rays.

F. S.

The Heterogeneity of β-Rays from a Thick Layer of Radium-*E*. J. A. GRAY and W. WILSON (*Phil. Mag.*, 1910, [vi], 20, 870—875).—Using a thick layer of radium-*D* and -*E*, it was found that, although the whole radiation was absorbed exponentially [$\lambda(\text{cm.})^{-1} = 43$] by aluminium, different bundles of rays of widely different penetrating power [$\lambda(\text{cm.})^{-1}$ from 13 to 62·5] could be sorted out by a magnetic field. When the rays had first to pass through aluminium, it was proved by magnetic deflexion measurements that the average velocity of the rays surviving was increased.

F. S.

The Deflexion by an Electrostatic Field of Radium-*B* on Recoil from Radium-*A*. SIDNEY RUSS and WALTER MAKOWER (*Phil. Mag.*, 1910, [vi], 20, 875—882).—Some, at least, of the atoms of radium-*B* recoiling from radium-*A* are positively charged, although in the disintegration of radium-*A* positively charged α-rays are also expelled. The "recoil atoms" from a wire made active by a deposit of radium-*A* were passed between oppositely charged plates in a vacuum and fall upon a metal cross-piece. The distribution of the activity on the latter was determined by moving it under a narrow slit in the base of an α-ray electroscope. The point of maximum distribution was shifted by the application of a field to the plates, and from the magnitude of the shift the charge carried by the "recoil atoms" was deduced, on the assumption that the velocity of the atoms was $3{\cdot}27 \times 10^7$ cm. per second, which is that calculated from the principle of equality of momentum of the two parts of a disintegrating atom.

The values obtained indicated that the recoil atom carries unit positive charge, and that its mass is 214, in agreement with what is to be anticipated from the disintegration theory. F. S.

The Deflexion by a Magnetic Field of Radium-*B* on Recoil from Radium-*A*. WALTER MAKOWER and E. J. EVANS (*Phil. Mag.*, 1910, [vi], 20, 882—886).—Similar experiments to those described in the preceding abstract were carried out, the "recoil atoms" being deviated in a magnetic instead of an electrostatic field. The distribution of the activity on the cross-piece was determined by laying it on a photographic plate, and then measuring the photograph obtained by projecting it on to a screen by means of a lantern. The value for $H\rho$ of the deflected "recoil atoms" was 6.52×10^5. This is twice that obtained by Rutherford for the α-particle of radium-*A*, and, since $H\rho = m/ve$, and the value of mv must be the same in both cases on the principle of equality of momentum, it follows that the charge carried is the unit charge instead of twice the unit charge, as in the case of the α-particle. By combining the results of the electrostatic and magnetic deflection measurements, it follows that the velocity of the "recoil atom" is 3.23×10^7, and its mass is 194 (H = 1), which is as close to the theoretical value 214 as can be expected. F. S.

Measurements of the Rate at which Helium is Produced in Thorianite and Pitchblende, with a Minimum Estimate of of their Antiquity. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, *A*, 84, 379—388).—A description is given of the methods employed to measure the rate of production of helium from solutions of thorianite (two varieties, one specially rich in uranium from the Galle district of Ceylon) in nitric acid, and of pitchblende. The latter was dissolved in nitric acid, and the insoluble sulphates converted into carbonates and dissolved to form a separate solution. The solutions were contained in large flasks closed by barometer tubes dipping beneath mercury, and the gaseous contents were removed periodically with steam by boiling the liquids. The volume of helium was estimated in the expelled gas after subjection to cooled charcoal in a narrow capillary tube. The rate of production of helium per gram of mineral per annum was found to be 3·7 ($\times 10^{-8}$ c.c.) for Galle thorianite, containing 24·5% of U_3O_8 and 65·44% of ThO_2; 2·79 for ordinary thorianite, containing 13·10% of U_3O_8 and 72·65% of ThO_2; and 3·16 for pitchblende, containing 37·6% of U_3O_8. These results are in good agreement with those calculated earlier on certain assumptions. The minimum ages of the two thorianites are 2·50 and 2·80 ($\times 10^{-8}$ years) respectively, as calculated from the period required to produce the contained helium, no allowance being made for the helium that escapes. The minimum ages of 4 minerals previously worked with are, in millions of years, (1) sphaerosidenite (Oligocene) 8·4, (2) hæmatite (Eocene) 31, (3) hæmatite (Carboniferous limestone) 150, (4) sphene (Archean) 710. F. S.

Disengagement of Emanation from Radium Salts. III. LÉON KOLOWRAT (*Le Radium*, 1910, 7, 266—269. Compare this vol., ii, 91).—With barium chloride containing only minute proportions

of radium chloride, the disengagement of emanation from the salt at a temperature θ, after a period of accumulation t from the moment of complete removal of emanation by fusing the salt, is the same whether the temperature is maintained at θ throughout or for only a short time at the end of the period of accumulation, and is represented by $c(1-\epsilon^{-\lambda t})/\lambda$, where λ is the constant of the emanation, and c a coefficient between 0 and 1, which is a function of θ, but independent of t; c may be considered as the fraction of the emanation generated retained by the solid salt at $\theta°$, and may be determined with consistency in different experiments at the one temperature for different times for the same preparation, but varies greatly with different preparations otherwise apparently similar. Impure preparations seem to have lower values of c than those only containing barium and radium chloride. The idea that part of the radium chloride is in the form of a solid solution in the barium chloride and gives up its emanation more readily than the rest supposed to be present with the barium chloride in the form of mixed crystals (Kolowrat, this vol., ii, 767) does not account for the differences, as there is no regular relation between the value of c and the proportion of radium present. Using a few thousandths of a milligram of pure radium chloride, it was found that heating to the fusion temperature no longer effected complete release of the accumulated emanation, the material being changed by high temperature into an insoluble and probably infusible product. This agrees with Mme. Curie's observation that heating reduces the escape of emanation from radium chloride, and was confirmed by observations on the minimum β-radiation attained by the preparations after heating. The 1% barium–radium chlorides are less easily changed by heat, and give up the whole of their contained emanation by fusion. F. S.

Action of Radium Emanation on Colloids. WILLEM P. JORISSEN and H. W. WOUDSTRA (*Chem. Weekblad*, 1910, 7, 941—948. Compare Henri and Mayer, Abstr., 1904, ii, 184).—The authors confirm the results obtained by Henri and Mayer in their work on the action of radium emanation on colloids. They find that the sensitiveness of a colloid towards an electrolyte is increased by this emanation. A. J. W.

The Diffusion of Gaseous Ions. ÉDOUARD SALLES (*Compt. rend.*, 1910, **151**, 712—714).—The coefficients of diffusion of ions in carefully dried air, carbon dioxide, nitrogen, and oxygen, produced by the α-rays of polonium, have been measured by a method the principle of which is due to Townsend. The values are in accord with those given by Townsend for ions produced in other ways, the positive ion for oxygen ($k=0·030$) being the only one in disagreement. Experiments under pressure p (mm. of mercury) showed for $p \times k$ constant values of about 22 for the positive, and 32 for the negative, ions in air and nitrogen. F. S.

Attempts to Prepare Metallic Radium. ERICH EBLER (*Ber.*, 1910, **43**, 2613—2618).—From 0·02 gram of barium bromide con-

taining 2·5% of radium bromide, about 1 mg. containing 9% was prepared by crystallisation, converted into carbonate, and dissolved in aqueous hydrazoic acid. On evaporation, a white, crystalline mass of radium azoimide, $Ra(N_3)_2$, containing barium azoimide was left. Previous experiments with barium azoimide had shown that it is not decom posed by the action of radium rays. The preparationwas brought into a narrow "melting-point tube," supported inside a perfectly exhausted glass tube, and heated in a special sand-bath very slowly to 180—250°. After some hours, a shining metallic mirror was formed, which was sealed off from the preparation, and found to contain 73% of the radium employed, by electroscopic measurements. The radium mirror was dissolved out of the tube and converted into chloride. In spite of the impurity of the preparation, the experiment proves that elementary radium is chemically and physically analogous to elementary barium. It appears to form nitride with moist air even more readily than barium. F. S.

The Radium Content of Waters of the Cam, Cambridge Tap Water, and Some Varieties of Charcoal. JOHN SATTERLEY (*Proc. Camb. Phil. Soc.*, 1910, **15**, 540—544).—The emanation generated per litre of Cambridge tap water and of Cam river water respectively is that in equilibrium with 130 and 5 ($\times 10^{-12}$ gram of radium), while the amount of radium is 1·6 and 3·2 ($\times 10^{-12}$ gram). The Cambridge waters are therefore richer in radium than those of Montreal, which accounts for the higher values found for the quantity of emanation in the air of Cambridge than in that of Montreal. In four varieties of charcoal, the radium contents per gram were: (1) cocoanut 0·4, (2) cocoanut 0·3, (3) Brazil-nut 1·3, (4) wood 0·3 ($\times 10^{-12}$ gram). F. S.

Investigations on the Radium Content of Rocks. I. ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam,* 1910, **13**, 359—365).—The investigation includes ten rocks from the West Coast of Sumatra, comprising quartz porphyrite, granite, basalt, andesite, augite-andesite, granitite, diorite, and diabase. These rocks showed a content of radium of the order of 10^{-12} gram per gram, similar in magnitude to those which have been examined by other investigators. The highest was a basalt from the volcano of Asar (13·0), and the lowest were the diorite and diabase ($0·3 \times 10^{-12}$ gram of radium per gram). F. S.

The Radium Content of Basalt. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, *A*, **84**, 377—379).—The discrepancy between the author's results and those of Joly on the radium content of igneous rocks is greatest in the case of basalts, the value found by the latter being about eight times that found by the former. New measurements with special precautions have therefore been made on a new set of three basalts, which give results even lower than the previous set (from 0·16 to $0·35 \times 10^{-12}$ gram radium per gram), whilst in one sample previously employed a new determination gives the same result as before (0·57). It is possible that Joly has met with exceptional specimens. F. S.

The Presence of Radioactive Elements in Some Incrustations from the Fumaroles of Vesuvius. GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli,* 1910, [iii*a*], **16**, 48—50. Compare Abstr., 1907, ii, 365).—Incrustations from recent fumaroles, dissolved in hydrochloric acid and precipitated with hydrogen sulphide, yield a mixture of sulphides, from which, after removing arsenic by ammonium sulphide, boiling with dilute hydrochloric acid, and dissolving in nitric acid, lead is removed as sulphate, and a greyish-white precipitate is then obtained by the addition of ammonia. This precipitate is markedly radioactive. C. H. D.

The Radioactivity of the Products of the Recent Eruption of Etna. ARNALDO PIUTTI and GENNARO MAGLI (*Rend. Accad. Sci. Fis. Mat. Napoli,* 1910, [iii*a*], **16**, 159—163).—The products of the recent volcanic eruption of Etna have been studied in the same manner as those of Vesuvius (this vol., ii, 290). The smallest radioactivity is possessed by the volcanic sands, followed in ascending order by the lava, the scoriæ, and the sublimed products and incrustations. The maximum activity agrees with that of the materials obtained from the preceding eruption, and is greater than that of corresponding materials from the last eruption of Vesuvius, in which, however, the same relative order is observed. C. H. D.

Radioactivity of Italian Minerals. RAFFAELO NASINI and MARIO G. LEVI (*Gazzetta,* 1910, **40**, ii, 101—122. Compare Abstr., 1909, ii, 7, 110).—A complete account of the work on this subject carried out by the authors and others. R. V. S.

A Determination of the Ratio of Mass to Weight for a Radioactive Substance. L. SOUTHERNS (*Proc. Roy. Soc.*, 1910, *A*, **84**, 325—344).—The ratio of mass to weight of the oxides of lead and of uranium have been compared by filling the hollow bob of a specially constructed rigid pendulum with these two substances, and no difference between them has been indicated. The ratio is the same for the two substances within one part in 200,000. F. S.

Electrical Purification and Conductivity of Liquid Sulphur Dioxide. J. CARVALLO (*Compt. rend.*, 1910, **151**, 717—719).—When a current is passed through liquid sulphur dioxide free from air between platinum electrodes, the difference of potential being V, it is found that the current I diminishes with time until a limit is attained. The negative electrode becomes slightly brown, and the liquid undergoes purification by prolonged passage of the current.

When V is 200—500 volts, the limiting current does not vary as a simple function of V. With a difference in potential of 1000 or 2000 volts, the current is much smaller than that passing with lower tensions. Curves plotted for $I=f(V)$ are in accordance with Ohm's law, when V does not exceed 100 volts. The limiting conductivity for higher voltages is not in agreement with this; the law governing it under these conditions appears to resemble the laws for the conductivity of gases, and will be further studied. The limiting specific

resistance under 100 volts was $7 \cdot 6 \times 10^9$ ohms; under 2350 volts, $4 \cdot 9 \times 10^{10}$ ohms, and under 4000 volts, $4 \cdot 9 \times 10^{10}$ ohms per cm.

W. O. W.

Electrical Conductivity of Solutions in Aniline, Methylaniline, and Dimethylaniline. AL. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 683—690).—The object of the research was to determine the connexion between the chemical nature of an amine and its dissociating power and its power of giving conducting solutions. Since the dielectric constants of the three amines are very close to one another, any difference that may exist in their dissociating powers would be due to the difference in their chemical constitutions. The following salts were employed: ammonium iodide, pyridine hydrobromide, aniline hydrobromide, silver nitrate, and lithium iodide, and tables and a curve for aniline solutions are given, showing the relation of concentration to electrical conductivity. All the solutions show a rapid diminution of their molecular electrical conductivity with increasing dilution, this probably being due to the formation and dissociation of complex salts, such as $NH_4I,2PhNH_2$, $AgNO_3,2PhNH_2$. Aniline gives the best conducting solutions, methylaniline comes next, whilst the solution in dimethylaniline seems to be on the border between conducting and non-conducting solutions. The conclusion is drawn that the chief factor determining the ability to give conducting solutions is the chemical constitution of the amine.

Z. K.

The Potential of the Sodium Electrode. GILBERT N. LEWIS and CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1910, **32**, 1459—1468). —A method of obtaining the difference of potential between metallic sodium and a solution of sodium ions of normal concentration is described. This consists in determining the potential difference between a dilute sodium amalgam and an aqueous solution of sodium hydroxide, and also the *E.M.F.* of the cell metallic sodium | sodium iodide dissolved in ethylamine | sodium amalgam. The *E.M.F.* of this galvanic combination is independent of the medium in which the sodium salt is dissolved, and ethylamine was chosen because it is not acted on by the alkali metal.

The *E.M.F.* of the combination sodium amalgam (0·206% sodium) | 0·2*N*-sodium hydroxide | normal calomel electrode was found to be 2·1986 volts. Assuming that the sodium hydroxide is ionised to the extent of 82·8%, this gives for the *E.M.F.* of the cell sodium amalgam | aqueous solution containing Na ions in normal concentration | normal calomel electrode, 2·1525 volts. The potential difference between sodium and 0·206% sodium amalgam is 0·8456 volt, and these data when combined give for the *E.M.F.* of the combination sodium | aqueous solution containing 1*N*-sodium ion | normal calomel electrode, 2·9981 volts at 25°.

The temperature-coefficient of the sodium–sodium amalgam cell is −0·0000408 volt per degree, and from this it is calculated that the heat of solution of 1 gram-atom of sodium in 0·206% sodium amalgam is 19,790 cal.

The precautions to be observed in the preparation of pure sodium

amalgam and of anhydrous ethylamine are described in detail. If these are followed, the observed potential differences can be reproduced with great accuracy. H. M. D.

Oscillographic Investigation of Some Electrolytic Processes. III. D. REICHINSTEIN (*Zeitsch. Elektrochem.*, 1910, **16**, 916—944. Compare Abstr., 1909, ii, 960).—Using a more sensitive oscillograph (on the photographic record a deflexion of 1 mm. on the ordinate axis is given by a current of 0·0004 ampere, whilst 1 mm. on the axis of abscissæ corresponds with 0·0006 second), the author has studied the polarisation of an electrode produced by a fairly strong current lasting a few hundredths of a second and its subsequent decay. The cases examined are the anodic and cathodic polarisation of platinum (also mercury and silver) in 28% sulphuric acid; the anodic polarisation of copper, silver, lead, and nickel in solutions of their salts, and the cathodic polarisation of palladium in sulphuric acid and in acid zinc sulphate. In all the experiments the experimental electrode is combined with a large, unpolarisable electrode. The results are, as a rule, given in the form of reproductions of the oscillograph curves. The main result, however, is that during the passage of the polarising current, the difference of potential between the electrode and the solution is always much larger than the equilibrium *P.D.* when no current is flowing, and the difference increases with the current. The rate of disappearance of this excess depends on the nature of the product of electrolysis and of the electrode. The phenomenon is met with in every case examined; it is hardly possible to give the details, and also the possible mechanisms which the author suggests in explanation of them in a brief abstract. It may be said, however, that the view is taken that the primary products of the electrolysis are not identical with the stable substances finally formed, the decay of the excess polarisation being due to the transformation of one into the other. T. E.

The Potentials of Chlorine, Bromine, and Iodine in Methyl and Ethyl Alcohol. J. NEUSTADT (*Zeitsch. Elektrochem.*, 1910, **16**, 866—869).—The *E.M.F.* of a cell Ag | saturated solution of AgCl | Cl is independent of the solvent used. It is given by $E = \epsilon_{Ag} - \epsilon_{Cl} + RT/nF(\log[Ag^{\cdot}] + \log[Cl'])$. The quantity in the brackets is the logarithm of the solubility product of silver chloride, and ϵ_{Ag} and ϵ_{Cl} are the normal potentials of silver and chloride in the solvent used. From the value of E for aqueous solutions and determinations of the solubility products of the silver haloids in the alcohols, the differences of the normal potentials of the haloids in alcoholic solutions are therefore easily calculated. The solubility products in alcoholic solutions are obtained by measurements on concentration cells of the type Ag | $0{\cdot}1N$-$AgNO_3$ | $0{\cdot}1N$-KCl saturated with AgCl | Ag. The concentrations of the silver and chlorine ions in the alcoholic solutions are calculated from the conductivity measurements of Dempwolff (Abstr., 1905, ii, 9). The mean values of the solubility products at 25° are:

	Methyl alcohol.	Ethyl alcohol.
AgCl	$1{\cdot}95 \times 10^{-13}$	$1{\cdot}85 \times 10^{-14}$
AgBr	$1{\cdot}1 \times 10^{-15}$	$6{\cdot}4 \times 10^{-16}$
AgI	$1{\cdot}5 \times 10^{-18}$	$1{\cdot}1 \times 10^{-19}$

The differences of the normal potentials, calculated in the way indicated above, are:

	Water.	Methyl alcohol.	Ethyl alcohol.
$\epsilon_I - \epsilon_{Br}$	0·467	0·418	0·471
$\epsilon_I - \epsilon_{Cl}$	0·772	0·707	0·712

Determinations in acetone were impossible, owing to formation of complex salts. T. E.

Heat Development of the Clark Cell. F. POLLITZER (*Zeitsch. physikal. Chem.*, 1910, **74**, 748).—Cohen (Abstr., 1900, ii, 520, 703) has calculated from the heats of solution, etc., that the heat development of the Clark cell is 81,127 cal., in fair agreement with the value calculated from the variation of the *E.M.F.* with temperature, 81,490 cal. In calculating the latter value, however, an incorrect value of the electrical equivalent of heat has been used. The accurate value of the latter (1 watt-second = 0·2387 cal.) gives 82,402 cal. at 18°, which does not agree with the value calculated from the heats of solution, etc. G. S.

Piezochemical Studies V. The Transition Element and its Applications. ERNST COHEN, KATSUJI INOUYE, and C. EUWEN (*Zeitsch. physikal. Chem.*, 1910, **75**, 1—29. Compare Abstr., 1909, ii, 981).—The transition temperature $ZnSO_4,7H_2O \rightleftarrows ZnSO_4,6H_2O + H_2O$ has been determined at intervals of pressure between 1 and 1500 atmospheres by means of so-called transition elements of two types. The first type, a modified Clark cell, was constituted as follows:

Electrode reversible with reference to anion.	Saturated solution of zinc sulphate in contact with the stable solid phase of the salt.	Electrode reversible with reference to cation.

The *E.M.F.* of this element under different pressures was measured at temperatures above and below the transition point, and the latter, at a definite pressure, taken as the point as which the curves representing the influence of temperature on the *E.M.F.* above and below the transition temperature intersected. The other arrangement consisted of two cells, one of which contained a saturated solution of zinc sulphate in contact with the stable form of the salt, whilst the solution in the other was in contact with the metastable form of the salt (the hexahydrate). The temperature at which the *E.M.F.* becomes zero when these cells are set in opposition is the transition temperature.

The transition temperatures with the first type of cell are 38·12°, 39·96°, 41·19°, and 42·63°, and with the second type 38·10°, 39·90°, 41·35°, and 42·80° at 1, 500, 1000, and 1500 atmospheres respectively. The result at one atmosphere pressure is only in moderate agreement with those of previous observers, but is fully confirmed by a dilatometer experiment (38·10—38·20°). G. S.

Piezochemical Studies. VI. ERNST COHEN and KATSUJI INOUYE (*Zeitsch. physikal. Chem.*, 1910, **75**, 219—231. Compare preceding abstract).—The effect of pressure on the *E.M.F.* of the cell of the second type already described (*loc. cit.*) has been determined indirectly by application of the equation: $E_\pi - E_0 = \pi(v_2 - v_1)$, where v_1 and v_2 represent the volumes of the system before and after

the passage of 96,540 coulombs, and π is the pressure. The factor $v_2 - v_1$ has been determined directly by putting pure zinc sulphate heptahydrate in a pyknometer, filling up with toluene as indifferent liquid, and finding the change of volume after transformation to the hexahydrate. Substituting in the above equation, the value $E_{500} - E_0 = 0·00088$ volt is obtained, as compared with the experimental value 0·00108 volt.

Further, the Clausius-Clapeyron equation:

$$dT/dp = 10,333T(\sigma - \mathrm{T})/427·2v,$$

where $(\sigma - \mathrm{T})$ is the change of volume in the transition of zinc sulphate heptahydrate, and v is the accompanying thermal effect, can be employed to find the effect of change of pressure on the transition temperature. Inserting the appropriate values of $(\sigma - \mathrm{T})$ and v, it is found that $dp/dT = 0·0032°$, whereas the experimental value is 0·0036°.

Finally, another equation is derived thermodynamically, by means of which dp/dT can be calculated by means of electrical measurements. It leads to the value of $dp/dT = 0·0027°$, instead of the experimental value given above. G. S.

Thermo-[electric] Forces of Solid Solutions of Metals and Schenck's Law. AUGUST L. BERNOULLI (*Ann. Physik*, 1910, [iv], **33**, 690—706).—Thermo-electric measurements have been made for various solid solutions of metals in order to test Schenck's formula $\pi = R/2e.\log(k'/\sigma' : k/\sigma)$, in which π is the thermo-electric difference of potential between the pure metal and a solid solution containing a second metal, k and σ are the thermal and electric conductivities of the solvent metal, and k' and σ' the corresponding quantities for the solution.

Solutions of thallium and tin in silver, of mercury in cadmium, and of tin, zinc and nickel in copper, were investigated. For sufficiently dilute solutions the observed thermo-electric potential difference agrees with that calculated from Schenck's formula, and this agreement is particularly good when the atomic weight of the solute metal is considerably greater than that of the solvent metal. As the concentration of the solutions increases, the agreement becomes less satisfactory. In the case of the copper zinc alloys, the observed potential differences are much larger than those obtained by calculation, and this is attributed to the formation of the compound Cu_2Zn_3. H. M. D.

Electrophoresis of Lamp Black. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1910, **24**, 345—354).—Using an apparatus similar to that described by Coehn (Abstr., 1909, ii, 841), the author has investigated the electrophoresis of lamp black (Kahlbaum's) which had been subjected to different methods of purification in order to obtain a suspension in water. These methods were: (*a*) treatment with a mixture of potassium dichromate and concentrated sulphuric acid for eighteen hours, and subsequent washing with dilute hydrochloric acid and finally with water; (*b*) trituration with concentrated sulphuric acid and then washing as in (*a*); (*c*) warming with a dilute

solution of sodium in ordinary alcohol, and subsequent washing with alcohol and water; (*d*) no purification was attempted, but a suspension was obtained directly by introducing the lamp black into dilute alcohol, which was slightly alkaline. Suspensions could not be obtained when it was put directly into water.

The suspensions obtained were investigated as such, and after the addition of enough potassium hydroxide or hydrochloric acid to make them from *N*/110 to *N*/11,000. All alkaline suspensions showed the phenomenon of anaphoresis, and were fairly stable. Suspensions which were very feebly acid still showed anaphoresis, but when the acidity was increased (*N*/110) they were flocculated so rapidly that it was impossible to observe whether they showed cataphoresis (compare Perrin, Abstr., 1905, ii, 138). Details are also given of actual stability of the different suspensions and of the effect of filtration.

The remainder of the paper is occupied with a discussion of the detergent action of soap, special reference being made to the theories of Spring (this vol., i, 6) and of Chevreul. T. S. P.

The Nature of the Coloured Films Formed on the Alkali Metals by Electric Discharges. JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1910, **11**, 1082—1083. Compare this vol., ii, 379). —The coloured substances which are formed on the surface of the alkali metals when subjected to the influence of the glow discharge in hydrogen at low pressure have been described as colloidal solutions of the metals in the corresponding hydrides. It is pointed out that the colours of the different substances are identical with those of the corresponding modifications of the alkali metals obtained by Fischer and Schröter (this vol., ii, 609) by the disintegrating action of the arc discharge on alkali metal electrodes immersed in liquid argon. The two series of coloured substances obtained by the two methods are considered to be identical.

The presence of hydrogen is supposed to facilitate the formation of the colloidal metals under the influence of the glow discharge by forming hydrides which act as solvents for the metals. Since hydrogen was in all probability present in the arc discharge experiments of Fischer and Schröter, the formation of the colloidal metals in these circumstances may be in some measure due to the preliminary formation of hydrides.

When potassium is subjected to the glow discharge at the temperature of liquid air, the coloured film is not formed to any appreciable extent, and this is attributed to the absence of the hydride, which is not formed in consequence of the low vapour pressure of the alkali metal at this temperature. H. M. D.

Specific Heats and Gas Equilibria from Explosion Experiments. II. MATHIAS PIER (*Zeitsch. Elektrochem.*, 1910, **16**, 897—903). —The manometer previously used (Abstr., 1909, ii, 789) is improved by fixing the mirror directly to the corrugated diaphragm about midway between its centre and its periphery.

By exploding acetylene (*a*) with excess of air, (*b*) with excess of

oxygen, and (*c*) with excess of carbon dioxide, data are obtained from which the ratios of the specific heats of carbon dioxide or of oxygen to that of nitrogen are calculated. The molecular heat of oxygen, up to 2200°, is the same as that of nitrogen ($4{\cdot}900 + 0{\cdot}00045t$). The formulæ of Holborn and of Langen do not represent the results obtained for carbon dioxide; a new equation is therefore proposed for the mean molecular heat of carbon dioxide between 0° and t° at constant volume: $c = 6{\cdot}800 + 3{\cdot}3 \times 10^{-3}t - 0{\cdot}95 \times 10^{-6}t^2 + 0{\cdot}1 \times 10^{-9}t^3$. This represents both the author's results between 1600° and 2100° and those of Holborn and Henning (200—1364°) with sufficient accuracy.

The molecular heat of sulphur dioxide is obtained from explosions of carbon disulphide with oxygen. It is the same as that of carbon dioxide up to 2000°.

The dissociation of carbon dioxide is calculated from the results of explosions of mixtures of carbon monoxide and oxygen on the assumptions that carbon monoxide has the same molecular heat as nitrogen, and that the above expression for carbon dioxide holds up to 3000°. The results are too high, which is taken to indicate that the specific heat of carbon dioxide increases more rapidly above 2000°. An attempt to measure the equilibrium $CO_2 + H_2 = H_2O + CO$ also failed for reasons which are not clearly understood. T. E.

Critical Phenomena of Ethyl Ether. F. B. YOUNG (*Phil. Mag.*, 1910, 20, 793—828).—Observations relating to the nature of the critical phenomena in ethyl ether are described and discussed in reference to Andrews's theory.

It has been frequently observed that when a liquid in contact with its vapour is heated to the critical temperature, the meniscus disappears, whilst the density of the liquid is still distinctly greater than that of the vapour, and that this difference of density may persist for a considerable time, even when the temperature is raised above the critical temperature. Various explanations of this have been offered, some of which attempt to reconcile it with Andrews's theory, whilst others regard it as evidence of the incompleteness of this theory.

The ethyl ether used in the experiments was purified as completely as possible, and elaborate precautions were taken to free it from traces of air, for observations made with different tubes containing extremely small quantities of gaseous impurities indicate that these may visibly modify the critical phenomena. The Jena glass tubes containing the ether were heated in an aniline vapour-bath, the temperature of which could be adjusted very exactly by regulation of the pressure. Sliding freely inside each tube was a bell-shaped piece of tubing sealed on to a closed tube containing iron filings, which enabled the bell to be raised or lowered by means of an electro-magnet. This arrangement was found to give a very delicate means of testing the contents of the tubes for traces of gaseous impurities.

The conclusion drawn from the observations is that the critical phenomena observed with the pure substance can be explained in accordance with Andrews's theory, and that the phenomena advanced in support of the insufficiency of this theory are to be observed only

in tubes which contain traces of impurities. The part played by hydrostatic pressure is, in all probability, negligibly small, and the differences in density which are observed on the disappearance of the meniscus are apparently due to slight differences in temperature.

From a study of the phenomena of opalescence, the author considers that the opalescence is not due to the formation of an emulsion, but to variations in the temperatures of the individual molecules, as has been supposed by Küster.

In an appendix, a vapour thermostat for experiments on critical phenomena is described. The vapour-jacket is connected with a large flask, which communicates with a closed mercury manometer. This is provided with a short arm, in which is a float which makes electrical contact with a platinum-tipped needle. When contact is made, a relay is actuated, and a current is sent through a coil of fine wire contained in the large flask. The heat developed causes the air to expand until the consequent rise of pressure breaks the contact. By wrapping the coil of wire in cotton wool, the change of pressure is made to take place less suddenly, and the mercury in the gauge is thus enabled to follow the change of pressure more closely.

H. M. D.

Influence of the Surface of a Solid Phase on the Latent Heat and on the Melting Point. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 677—680. Compare Abstr., 1909, ii, 19, 295).—The formula obtained by the author connecting the melting point with the surface energy of a phase is now deduced by another method, and a further formula is given showing in what direction the melting point of small particles varies as compared with that of large ones. If small particles have a smaller heat of fusion, then the temperature at which they melt is lower than that of the large particles; if their heat of fusion is greater, then the melting point is higher than that of the large ones.

If the free surface energy of a solid phase is less than the free surface energy of the liquid phase, then the increase of surface of the solid phase is accompanied by a rise in its heat of fusion, and vice versa. If the free surface energy of the solid and liquid phases are equal, then the change in the size of the surface exerts no influence on the latent heat of fusion (see further, this vol., ii, 1043). Z. K.

Influence of Degree of Dispersion of Solid Crystalline Substances on their Melting Points. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 647—653).—A short discussion of the author's previous work on this subject. The properties of the surface layer of a crystal resemble, although they are not identical with, those of the interior of a strongly compressed liquid, whilst the superficial layer of a liquid resembles the interior of a strongly compressed gas; therefore, with an increase in the degree of dispersion, a solid, crystalline substance becomes more active chemically, more volatile, more soluble, and more readily fusible. The two most important factors in determining the structure and properties of the surface layer of a crystal are: (*A*) the unilateral action of the vectorial molecular forces

on the molecules, forming the free surface of the crystal. (*B*) The dynamic (kinetic molecular) processes occurring on the free surface of the crystal. *A* gives rise to the capillary pressure, which is superadded to the external pressure on the surface, and increases with the degree of dispersion; consequently, as the degree of dispersion increases, so *A* tends to diminish the similarity between the surface of the crystal and a liquid, the melting point, in general (except in cases such as ice), rising with an increase in pressure. *B*, on the other hand, tends to increase the similarity between the surface of a crystal and a liquid, and since a fine disperse system is almost always more active than a coarse one, *B* acts as a more energetic factor than *A*. In addition, the melting point is lowered in a system of great dispersion by the fact that the surface of the crystals dissolves the surrounding medium until saturated; consequently, the melting point and other physical properties of a disperse system varies with the nature of the medium by which it is surrounded, or from which the crystals have been separated, and the greater the degree of dispersion the more marked is this variation. Z. K.

The Spontaneous Crystallisation and the Melting- and Freezing-Point Curves of Mixtures of Two Substances which form Mixed Crystals and Possess a Minimum or Eutectic Freezing Point. Mixtures of Azobenzene and Benzylaniline. FLORENCE ISAAC (*Proc. Roy. Soc.*, 1910, *A*, **84**, 344—369).—From freezing- and melting-point observations with mixtures of azobenzene and benzylaniline, it has been found that these substances form a eutectic mixture which solidifies at 26° and contains 19% of azobenzene. Mixed crystals are formed by mixtures containing more azobenzene than the eutectic, but not by mixtures which contain less. The form of the melting-point curve was confirmed by analysis of the mixed crystals.

The temperatures at which different mixtures undergo spontaneous crystallisation were also determined by two different methods, and in this way the supersolubility curve was obtained. This curve exhibits a minimum for liquids which have approximately the composition of the eutectic mixture, and, for the most part, it runs nearly parallel to the freezing-point curve. The supersolubility curve, on the other hand, cuts the melting-point curve at three different points. The mixed crystals which separate out on spontaneous crystallisation along the supersolubility curve have been determined for various liquid mixtures of the two substances. Microscopic examination of sections cut from the solid solutions indicates that gradual changes take place in these mixed crystals at the ordinary temperature. H. M. D.

Freezing Mixtures. JACQUES DUCLAUX (*Compt. rend.*, 1910, **151**, 715—716).—A description of a simple method for attaining low temperatures. Two liquids, which produce a fall in temperature on mixing, are allowed to flow through two long glass tubes (diameter, 1 mm.). The liquids leave the tubes at the rate of 1 to 2 drops per second, and then mix. The mixture is caused to flow over the tubes before leaving the apparatus, thus lowering the temperature of the incoming liquids. By this method a temperature of −48° can

be maintained for long periods, employing 100 c.c. of carbon disulphide and 70 c.c. of acetone per hour. In one experiment, a volume of 20 c.c. was kept at $-43·5°$ with this mixture in a double-walled, silvered glass tube, the external temperature being 22°. W. O. W.

Condition of Substances in Solution in Absolute Sulphuric Acid. V. GIUSEPPE ODDO and E. SCANDOLA (*Gazzetta*, 1910, **40**, ii, 163—209. Compare Abstr., 1909, ii, 377, 792, and Hantzsch, *ibid.*, ii, 973).—Since in the opinion of the authors the condition of alcohols in solution in absolute sulphuric acid has now been settled, they have proceeded to the study of the ethers and esters. In a polemical appendix, the objections raised by Hantzsch are discussed, further inaccuracies in his results are suggested, and finally the authors' views on the whole question under examination are set forth.

In calculating from the cryoscopic measurements the molecular weights of the substances in solution, a correction is introduced for the proportion of the dissolved substance which has been acted on by the sulphuric acid, the correction being obtained by neutralising the remaining sulphuric acid with barium hydroxide and weighing the barium sulphate obtained. When this is done, it is found that the molecular weights amount to very nearly 50% of the theoretical in the case of all the following ethers: ethyl ether, propyl ether, *n*-butyl ether, *iso*amyl ether, *n*-heptyl ether, dimethylpyrone. Hence all these ethers yield an acid oxonium sulphate which dissociates.

In the case of the esters ethyl acetate and ethyl monochloroacetate, it is found that decomposition (to the extent of 15·35% and 32·9%, respectively) occurs, although Hantzsch has stated otherwise in regard to the former substance. Taking this decomposition into account, the molecular weights are 55% and 62% respectively of the theoretical values, showing that the esters are weaker oxonium bases than the ethers, the weakness being greater the more negative the radicle which they contain. The authors consider that when an ester is dissolved in absolute sulphuric acid, three changes occur: (1) formation of the acid oxonium sulphate, which dissociates into two ions; (2) molecular dissociation of part of this salt; (3) partial decomposition of the ester into two acids, namely, the alkyl hydrogen sulphate, and the acid corresponding with the contained radicle. Of these, the second tends to give values above 50%, the third values below that. Hence the mere cryoscopic measurement may indicate 50%. Results according with this view were obtained also with *iso*amyl formate, *iso*amyl acetate, and *iso*amyl butyrate.

Experiments with ethyl nitrate, *iso*amyl nitrate, and *iso*amyl nitrite show that with increase in the negative character of the acid radicle (as compared with those of the ethers and esters already mentioned), the acid decomposition of the molecules reaches a maximum, and no indication of an oxonium salt can be found. *sec.*-Butyl nitrate gives results indicating that the difference between primary and secondary alcohols already noticed (*loc. cit.*) exists also in the case of the esters. Methyl sulphate has not the normal molecular weight, as stated by Hantzsch On the contrary, the authors advance reasons for supposing that a large part of it is decomposed to form the

acid ester, and that in addition complex molecules, such as $Me_2(HSO_4)_2$, also exist in the solution. R. V. S.

Some Molecular Weights in Phosphoryl Chloride as a Cryoscopic Solvent. PAUL WALDEN (*Zeitsch. anorg. Chem.*, 1910, **68**, 307—316).—Phosphoryl chloride has been used as a cryoscopic solvent by Oddo (Abstr., 1901, ii, 492,; 1904, ii, 236), who found the melting point to be $-1·782°$, and the cryoscopic constant 70·16. The author finds the melting point to be $+1·25°$, and the cryoscopic constant, determined as the mean of experiments with several compounds, 76·8, corresponding with a latent heat of fusion of 19·8 Cal.

Simple molecular weights are given by the compounds ICl, ICN, N_2O_5, Cl_2O_7, and OsO_4. Phosphoric oxide, chromic acid, and iodine pentoxide are practically insoluble in phosphoryl chloride.

The cryoscopic constant of bromoform is 144. Both solid α- and liquid β-iodine chloride are unimolecular in bromoform. C. H. D.

Di*cyclo*hexyl as a Cryoscopic Solvent. LUIGI MASCARELLI and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 410—414).—For the purpose of comparison with *cyclo*hexane (Abstr., 1909, ii, 19, 972) the behaviour of di*cyclo*hexyl, $C_6H_{11}·C_6H_{11}$, prepared by the reduction of diphenyl by hydrogen in the presence of nickel, has been examined. The cryoscopic constant has a mean value of 145·2. The solubility of most substances in this solvent in the cold is small. Phenol, propyl alcohol, and acetic acid are associated, even in dilute solution. The general behaviour of ketones and nitro-compounds in di*cyclo*hexyl closely resembles that of the same substances in *cyclo*hexane. Tetranitromethane, however, is normal. C. H. D.

Vapour Pressure Curves. DEMETRIUS E. TSAKALOTOS (*Zeitsch. physikal. Chem.*, 1910, **75**, 743—746. Compare this vol., ii, 266).—The minimum of vapour pressure in the binary mixture chloroform–ethyl ether is probably connected with the formation of a compound $Et_2O:CHCl_3$. From the results of surface-tension and vapour pressure measurements, it appears that liquid oxygen is polymerised, whereas according to Walden's boiling-point formula (Abstr., 1909, ii, 122) it is unimolecular. G. S.

Studies in Vapour Pressure. III. A Static Method for Determining the Vapour Pressures of Solids and Liquids. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, **32**, 1412—1434; *Ann. Physik*, 1910, [iv], **33**, 971—978. Compare this vol., ii, 687, 688).—The sources of error involved in vapour pressure measurements are discussed, and a critical résumé is given of the various methods which have been employed in such determinations. A new form of apparatus, called the *static isoteniscope*, is described, and it is claimed that by means of this apparatus more trustworthy measurements of vapour pressures can be made than by the older methods. It consists of a small U-tube, one limb of which is connected with a small spherical bulb, and the other with a long vertical tube, which communicates with a mercury

gauge and with a large iron bottle, which in turn can be put into communication with (1) the atmosphere, (2) a vacuum reservoir and water pump, or (3) a pressure reservoir and compression pump. The lower half of the U-tube is occupied by a confining liquid, and to prevent the ascent of this into the spherical bulb containing the vaporising liquid or into the long vertical tube, small bulbs are blown on the upper end of each limb of the U-tube. The liquid under investigation may be conveniently employed as confining liquid.

In the manipulation of the apparatus, the temperature of the liquid bath, in which the isoteniscope is immersed, is fixed, and the pressure in the iron bottle is then adjusted until the liquid in the bulb boils freely. After the removal of all air and dissolved gases, the pressure is cautiously increased until the levels of the confining liquid are the same in both limbs of the U-tube. To ensure that all foreign gases have been expelled, the process of boiling and adjusting of the pressure is repeated until constant pressure values are recorded on the gauge.

To test the results obtainable with this apparatus, the authors have measured the vapour pressure of water between 50° and 90°, the isoteniscope being immersed in a thermostat, the temperature of which was determined by means of a resistance thermometer. The data obtained are in close agreement with the measurements of Holborn and Henning. H. M. D.

Studies in Vapour Pressure. IV. A Re-determination of the Vapour Pressures of Mercury from 250° to 435°. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, **32**, 1434—1447; *Ann. Physik*, 1910, [iv], **33**, 979—988).—The measurements were made by means of the static isoteniscope (compare preceding abstract). From the vapour pressures, 106·52 mm. at 264·16°, 760 mm. at 356·95°, and 2598·67 mm. at 433·96°, a Kirchoff-Rankine-Dupré formula has been obtained, which may be written: $\log p = 9{\cdot}9073436 - 3276{\cdot}628/\theta - 0{\cdot}6519904 \log \theta$. The experimental data, which agree well with the pressures calculated from this equation, are compared with the older measurements of Gebhardt, Regnault, Ramsay and Young, and with the probable values calculated by Laby (Abstr., 1908, ii, 1039) from the several known series. The divergences between the authors' measurements and the values adopted by Laby are not inconsiderable, the difference amounting to 15 mm. at 450°.

A table is given showing the vapour pressures of mercury for every 2° between 0° and 450°; these pressures are the values obtained from the formula given above. The temperatures refer to the thermodynamic scale, and the pressures to the normal value of gravity.

H. M. D.

Studies in Vapour Pressure. V. A Dynamic Method for Measuring Vapour Pressures, with its Application to Benzene and Ammonium Chloride. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, **32**, 1448—1459; *Ann. Physik*, 1910, [iv], **33**, 989—994).—The authors describe a modified form of

apparatus for the dynamic measurement of vapour pressures (compare this vol., ii, 687, 688). The apparatus, which is immersed in a well-stirred liquid bath, consists of a small bulb, which communicates through a narrow tube with a small reservoir containing a suitable confining liquid. The tube is sealed through the upper wall of the reservoir, and terminates beneath the surface of the confining liquid. By means of a long vertical tube, the reservoir can be put into communication with a pump or compression apparatus.

This so-called *dynamic isoteniscope* has been employed for the measurement of the vapour pressure of benzene between 65° and 120°, and that of ammonium chloride between 280° and 333·5°. The results are compared with those of previous observers, who have used both static and dynamic methods of measurement. In the case of ammonium chloride, the authors' vapour pressure curve lies between the curves representing the data of Ramsay and Young and those of Johnson (Abstr., 1908, ii, 157). H. M. D.

The Composition and Vapour Tension of Solutions. III. The Influence of Temperature on the Composition of Solutions. M. S. Vrevsky (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 702—714).—The solutions of ethyl, methyl, and propyl alcohol in water have been investigated. Curves are given showing the relation between the % molecular composition of the solutions and the % molecular composition of the vapour at various temperatures for each pair of liquids, and the composition of the constant boiling point solution of propyl alcohol and water is deduced graphically. As the temperature of the solution of methyl and ethyl alcohol in water rises, the relative proportion of water in the vapour increases, whilst in the case of propyl alcohol, the proportion of alcohol in the vapour increases under similar conditions. These facts are deduced theoretically and shown to agree with experiment. Z. K.

Micro-distilling Apparatus. A. Gawalowski (*Zeitsch. anal. Chem.*, 1910, **49**, 744—745).—The apparatus consists of a very small flask (or test-tube), the neck of which is shaped like the head of an alembic. For very volatile liquids, by means of a cork, a small, inverted condenser is attached, the tube from which is bent slightly so that the liquid which drops from it will fall into the annular space in the alembic head. L. de K.

Measurement of Heats of Combustion with the Calorimetric Bomb and Platinum Resistance Thermometer. Franz Wrede (*Zeitsch. physikal. Chem.*, 1910, **75**, 81—94).—A number of other determinations of heats of combustion has been made by the method already described (Abstr., 1908, ii, 155). The heats of combustion in joules per gram are as follows: phenylacetic acid, 28·618; α-methyl glucoside, 18·175; naphthalene, 40·314; furoin, 23·941; glycine, 13·035; *dl*-alanine, 18·218; *d*-alanine, 18·217; *dl*-valine, 25·045; glycine anhydride, 17·441; *d*-alanine anhydride, 23·163; *dl*-leucylglycine, 24·367; formyl-*dl*-leucine, 24·134; diglycylglycine, 15·732; triglycylglycine, 16·119; glycylglycinecarboxylic acid, 11·234; methyluracil, 18·688; and *iso*serine, 13·709.

The sources of error in the work of previous observers, and the possibility of applying corrections to their data are discussed.

G. S.

Solutions. II. Variation of Density of Binary Mixtures with Temperature. F. SCHWERS (*Bull. Soc. chim.*, 1910, [iv], **7**, 937—940).—In previous papers (Abstr., 1909, i, 80, ii, 794) it has been shown that if changes of volume are expressed in percentages of the initial volume, the volume-temperature curve for a binary liquid mixture is sinuous and shows characteristic inflexions. It can be superposed on that illustrating the relationship between refractive index and temperature for the same mixture (this vol., ii, 913), and is similar in form to the curve expressing the relationship between heat developed and temperature of admixture, for the same mixture. These observations cannot be explained by the hydrate theory of solutions, and the following explanation is suggested. Admixture of two liquids may cause disintegration of associated molecules, the existence of which was proved by Ramsay and Shields (Trans., 1893, **63**, 1089). Such disintegration causes, according to van Laar (Abstr., 1900, ii, 189), a diminution in volume. In a mixture this may be counterbalanced in part, or overbalanced, by an increase in volume due to a new association between different molecules. In raising the temperature of such a system, each complex formed will undergo disintegration in accordance with its own constant of dissociation, and since this constant is not a linear function for a single liquid, it is conceivable that such changes occurring in a mixed system may be represented by a sinuous curve.

T. A. H.

New Theory of Molecular Volumes. GERVAISE LE BAS (*Chem. News*, 1910, **102**, 226—229).—The volumes of a number of atoms or groups in straight chain compounds or in the side chains of ring compounds have been calculated as described in previous papers (compare Abstr., 1907, ii, 754; 1908, ii, 667). The results are as follows: $OH = 11{\cdot}1 = 3H$; $CO{\cdot}OH = 37{\cdot}0 = 10H$; $CO_2 = 33{\cdot}3 = 9H$; $CO = 22{\cdot}2 = 6H$ (except in $CO{\cdot}OH$ group, where $CO = 25{\cdot}9 = 7H$); $CHO = 25{\cdot}9 = 7H$. Oxygen in the hydroxyl group generally, in the phenolic ethers, and in aldehydes and ketones $= 2H$; in the carbonyl group and in the aliphatic ethers it is equal to 3H. Doubly linked oxygen in a ring is also equal to 3H.

The volumes of a number of ring compounds containing oxygen are tabulated, and it is shown that ring structure is accompanied by considerable contraction, which varies in magnitude with the size and complexity of the ring. The relative volumes are, however, the same in spite of the contraction.

G. S.

Method for Determining the Lower and Upper Limits of Elasticity. The Hardening of Metals. O. FAUST and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1910, **75**, 108—126).—The lower limit of elasticity of a metal can be determined by subjecting a piece of which one side is highly polished to pressure or to a pull, and observing microscopically the point at which the polish just begins to disappear. The elasticity can be increased by alternately slowly

increasing the pressure beyond the first limit of elasticity, and then releasing, until finally an upper limit of elasticity, corresponding with the limiting pressure which produces flow in the metal, is reached. The metal has, tharefore, been hardened by slowly increasing the pressure. Some of the data for the lower and upper limits of elasticity are as follows: lead, lower limit 25 kilog./cm.^{2}, upper limit 102 kilog./cm.^{2}; zinc, drawn, lower limit 75, upper limit 770 kilog./cm.^{2}; copper, drawn, lower limit 1200, upper limit 2780 kilog./cm.^{2}. The lower limit depends greatly on the previous treatment of the sample.

The hardening of metals is ascribed, not to formation of a harder crystalline form, or to a change to the amorphous condition, but to a diminution in the size of the crystallites of which the metal is composed, owing to the formation of systems of sliding surfaces. The hardening is, therefore, a preparation for flowing, the latter occurring when the systems of sliding surfaces have sufficiently increased. Detailed evidence in favour of this view of hardening is advanced.

G. S.

Viscosity of Isodynamic and Motoisomerides. FERDINAND B. THOLE (*Zeitsch. physikal. Chem.*, 1910, 74, 683—686).—Mühlenbein (*Dissertation*, Cöthen, 1907) has found that the densities and viscosities of nitrobenzene and of quinoline altered on keeping, and ascribed this result to the existence of these compounds in two isomeric forms. The author has prepared pure specimens of these compounds, and finds no difference in the viscosities or densities immediately after distillation, and after twenty-two hours. For nitrobenzene, D_4^{25} 1·1987, viscosity at 25° = 0·018224; for quinoline, D_4^{25} 1·08994, viscosity = 0·033724.

The statement of Schaum (Abstr., 1898, i, 629) that the density of ethyl acetoacetate alters when kept is confirmed; the viscosity alters in a corresponding manner. The viscosity of the diethyl derivative of this ester, which cannot have an enolic constitution, and of ethyl malonate did not alter on keeping. G. S.

Viscosity of Albumin Solutions. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1910, 28, 353—354).—Polemical against Pauli and Wagner (this vol., ii, 830). The author maintains the validity of his measurements of the isoelectric point. G. S.

Influence of Chemical Affinity in Certain Adsorption Phenomena. LÉO VIGNON (*Compt. rend.*, 1910, 151, 673—675; *Bull. Soc. chim.*, 1910, [iv], 7, 985—988. Compare this vol., ii, 272, 273, 692).—The phenomena of adsorption may be divided into two classes, those due to attraction between chemically inert substances in colloidal solution or in suspension, and those due to chemical affinity between two substances, one of which is insoluble whilst the other is in true solution, or between two insoluble substances having some degree of chemical activity. Thus inert compounds, like calcined silica or asbestos, have no attraction for picric acid in aqueous solution, whilst in the case of zinc oxide or aluminium hydroxide the acid is adsorbed. Quartz adsorbs the alkali hydroxides or carbonates, but not the

chlorides of sodium or magnesium. Brigg's results (Abstr., 1906, ii, 13) are discussed from this point of view. W. O. W.

Adsorption of Gases by Charcoal. ALEXANDER TITOFF (*Zeitsch. physikal. Chem.*, 1910, **74**, 641—678. Compare Homfray, this vol., ii, 771).—The adsorption of hydrogen, nitrogen, carbon dioxide, and ammonia by cocoanut charcoal has been measured between $-79°$ and $+151·5°$ by the usual method. Between $-80°$ and $+80°$ the adsorption of hydrogen follows Henry's law, while the behaviour of the other gases at constant temperature is represented by the familiar formula $a_t = ap_t^{1/n}$, where a_t represents the amount of gas adsorbed at the pressure p_t, and a and $1/n$ are constants. When both pressure and temperature are varied, the results are represented by the formula $\log a_t = \log a_0 - (x - y\log p)t$, where x and y are constants bearing a simple relationship to a and $1/n$. Deviations from these formulæ occur in the cases of carbon dioxide and ammonia at the higher pressures, under which conditions the gases are probably partly liquefied. Ammonia was adsorbed to the greatest extent; at 0° and 10 cm. pressure, 1 gram of charcoal adsorbed 71 c.c. of this gas.

The heats of adsorption, q, of nitrogen, carbon dioxide, and ammonia gases were determined by means of an ice calorimeter. The mean values of q at 0° for 1 c.c. of gas are as follows: nitrogen 0·203 cal., carbon dioxide 0·31 cal., and ammonia 0·386 cal., each about 50 cm. pressure, the results for the last two gases being in good agreement with those obtained by Chappius (Abstr., 1883, 702). The values of q diminish considerably with increasing pressure. The heats of absorption have also been calculated from the isothermal adsorption curves by means of the formula $-q = nRT^2(x \times y\log p)/22·4\log_e$, and there is fair agreement between the calculated and experimental values. G. S.

Absorption of Gases by Charcoal. IDA F. HOMFRAY (*Zeitsch. physikal. Chem.*, 1910, **74**, 687—688. Compare this vol., ii, 771).—A few slight corrections to the former paper (*loc. cit.*) and some additional references are given. G. S.

Adsorption of Solutions [by Charcoal]. GERHARD C. SCHMIDT (*Zeitsch. physikal. Chem.*, 1910, **74**, 689—737. Compare Abstr., 1895, ii, 39).—In the great majority of the experiments the adsorption of acetic acid from aqueous solution was studied. The rapidity with which equilibrium is established depends on the nature of the charcoal; with some specimens it is practically instantaneous at room temperature. At low temperatures, the equilibrium is reached very slowly; increase of temperature enormously accelerates the adsorption. This is due, at least in part, to the more rapid removal of gases adsorbed (chiefly air) in the fine pores of the material as the temperature is raised. When equilibrium is attained, and the solution then diluted, the new equilibrium point is rapidly reached, the rate being the greater the more the concentration is altered. If, on the other hand, a more concentrated solution is added to a system already in equilibrium, the new equilibrium point is only slowly attained.

It is shown by experiments with acetic acid in aqueous solution

that on gradually increasing the concentration a maximum of adsorption is reached, a fact which shows that the usual adsorption formulæ cannot be valid within wide limits. A new formula, $\log[S/(S-x)]-Ax=C(a/v)$, is derived, S representing the maximum of adsorption, x the amount adsorbed, a the total amount of the solute, v the volume, and A and C are constants depending on the amount and nature of the coal. This formula represents the experimental results fairly satisfactorily. There are, therefore, three determining factors in adsorption: S, the maximum adsorption, K (proportional to C), the activity coefficient of the material, and A, which is a measure of the falling off in the attraction between absorbing surface and solute as the amount adsorbed increases.

From experiments with iodine and acetic acid in chloroform solution it is shown that the amount of two dissolved substances adsorbed from a solution containing both is less than the sum of the amounts adsorbed separately. Further, when charcoal is in equilibrium with one solute, and a second is added, it partially displaces the first substance from combination.

Some experiments on the adsorption of acetic acid from solution in ethyl acetate are described. G. S.

Dissociation of Ferric Sulphate. MAX BODENSTEIN and TATSUJI SUZUKI (*Zeitsch. Elektrochem.*, 1910, **16**, 912—916).—The measurements of Wöhler, Plüddemann, and Wöhler (Abstr., 1908, ii, 290) of the partial pressure of sulphur trioxide in equilibrium with ferric sulphate gave values three or more times larger than those of Keppeler and D'Ans (Abstr., 1908, ii, 289). The authors have therefore repeated both sets of experiments, taking every precaution to avoid accidental errors, and have obtained results which agree very well with the original measurements in both cases. In Wöhler's method the total pressure of the mixture of sulphur di- and tri-oxide and oxygen evolved by the heated ferric sulphate is measured, and the partial pressure of the trioxide calculated from Bodenstein and Pohl's measurements of the equilibrium constant. It is shown that the gases really are in equilibrium, and that this method of calculation is therefore justified. On the other hand, in Keppeler's method of passing air or nitrogen over the heated ferric sulphate, although the partial pressure of trioxide found is independent of the velocity of the gas within the rather narrow limits tried, the ratio between the oxides of sulphur and the oxygen is not in agreement with Bodenstein and Pohl's measurements of the dissociation of sulphur trioxide; there is always too little trioxide. The deviation diminishes as the temperature rises. It appears therefore that the low results obtained in Keppeler's experiments are due to equilibrium not being established. If ferric sulphate dissociates directly into ferric oxide and sulphur trioxide, an excess of trioxide would be anticipated instead of a deficit, hence the mechanism of the reaction is probably more complicated.

T. E.

The Theory of Transpiration, Diffusion, and Thermal Conduction in Rarefied Gases. MARYAN SMOLUCHOWSKI (*Bull. Acad. Sci. Cracow*, 1910, **7A**, 295—312).—The paper consists of three

sections. The first and second are concerned with a criticism of Knudsen's recent papers on the dynamics of rarefied gases (Abstr., 1909, ii, 216; *Ann. Physik,* 1910, **31**, 205, 633) from the theoretical standpoint. It is stated that the treatment of the problems is invalidated by the neglect to take into account the modification of the Maxwell-Boltzmann law of distribution of velocities during thermal conductivity and diffusion. An expression is deduced for the increase of thermal conductivity of gases produced by molecular surface currents. An analysis for the condition of low pressure, where the mean free path of the molecule is large compared with the dimension of the vessel, leads to results somewhat similar to those of Knudsen, but, it is claimed, by a simpler and more rigorous method. The last section contains a discussion of the experimental results of Soddy and Berry on the conduction of heat through rarefied gases (this vol., ii, 180). An exact calculation of the theoretical conduction of heat gives as the result that their values should be multiplied by the factor $\sqrt{\pi/6}=0{\cdot}7236$, and by the term $1-\beta/1+\beta$, where β is a coefficient representing the fraction of the total number of molecules "reflected" from the surface without change of kinetic energy. A re-calculation of their results shows that β can never be neglected, the interchange of energy between the surface and the molecule impinging upon it being the less perfect the lighter the molecule and the greater its intramolecular energy. F. S.

Methods of Investigation of Capillary-chemical Problems. P. N. PAWLOFF (*Zeitsch. Chem. Ind. Kolloide,* 1910, **7**, 265—267).—From a consideration of surface-energy relationships, von Weimarn arrived at the conclusion that a substance in a very fine state of subdivision should melt at a higher temperature than that found for the substance in the form of coarse particles. Since this conclusion is contradicted by experiment, some doubt has been thrown on the validity of the deductions made on the basis of surface-energy considerations. The author points out that the conditions under which a melting-point determination is carried out in the ordinary way preclude the possibility of observing the effect which is to be expected on the basis of Laplace's theory of capillarity.

von Weimarn's views relative to the nature of the surface layer of crystalline substances are also criticised. The assumption that the properties of the surface layer approximate to those of the inner layers of a highly compressed liquid is tantamount to the view that the surface layer is isotropic, whereas the geometric and physical characteristics of crystalline substances indicate that the surface layer is anisotropic (compare this vol., ii, 1033). H. M. D.

Osmotic Equilibrium between Two Fluid Phases. L. GAY (*Compt. rend.,* 1910, **151**, 754—756. Compare this vol., ii, 935).—The mathematical considerations advanced in a previous paper lead to the proposition that for two fluid phases in osmotic equilibrium with a common constituent at infinite dilution, at the same temperature and pressure, the variations in volume and thermal effects should be equal

whatever the temperature and pressure. Some theoretical consequences of this conclusion are discussed in the present communication.

W. O. W.

Diffusion [of Dissolved Substances]. OSCARRE SCARPA (*Nuovo Cimento*, 1910, [v], **20**, 212—225).—Vanzetti (Abstr., 1908, ii, 20, 88; 1909, ii, 978) has compared the coefficient of diffusion of certain electrolytes by allowing them to diffuse towards each other in a capillary tube filled with distilled water, and finding (for example, with silver nitrate and alkali chlorides) where a precipitate begins to appear. The author has deduced an equation which permits of the calculation of the coefficient of diffusion of one of the electrolytes in terms of that of the other, of the concentrations of the two electrolytes, and of the position in the tube where the precipitate begins to form.

It is shown that some of the assumptions of Vanzetti, for example, that the distances traversed by the salts are proportional to the coefficients of diffusion, are untenable. The values of the diffusion coefficients obtained by the above method agree neither with the theoretical values nor with those determined by the standard methods; the method is therefore not adapted to the study of diffusion.

The suggestion of Vanzetti that certain of his results are due to the hydrolysis of sodium chloride and other salts in very dilute solution is shown to be untenable. An equation is given which permits of the calculation of the hydrolysis of a salt of a strong base and a strong acid, and it is shown that the degree of hydrolysis is almost independent of the dilution, and therefore the quantity of salt hydrolysed diminishes with dilution, whereas Vanzetti has assumed that it increases.

G. S.

Fundamental Law for a General Theory of Solutions. EDWARD W. WASHBURN (*J. Chim. Phys.*, 1910, **8**, 538—568. Compare this vol., ii, 391).—The interdependence of the colligative properties of solutions (osmotic pressure, b. p., f. p., vapour pressure, etc.) follows from the laws of thermodynamics, and has no bearing on the question of the actual condition of solvent and solute. An ideal solution is one in which neither association nor dissociation of the solute nor association of solute with solvent (solvation) occur. In dilute solutions the molecular concentration of the solute is unaffected by solvation, so that dilute solutions of substances which neither associate nor dissociate behave as ideal solutions. The author develops the following general equation of state for solutions, which, whilst closely related to that advocated by van Laar, is expressed in terms of colligative properties rather than thermodynamic potentials: $d\pi = (-RT/V)d\log N$, where π is the osmotic pressure, V the molecular volume, and N the molecular concentration of the solvent.

Physical properties in ideal solutions or mixtures are additive. The vapour tension of any volatile component, such as the solvent $p = p_0 N$, where p_0 is the tension of the pure component. This rule is known to hold in the case of many mixtures of analogous organic substances, such as were examined by Young (Trans., 1903, **83**, 68).

Somewhat complex expressions are deduced for freezing point, boiling point, and the effects of concentration and temperature on chemical equilibrium in ideal solutions.

These laws of ideal solution apply to dilute solutions and to certain liquid mixtures, but in most concentrated solutions they are set aside by the unknown factors of association, and dissociation. R. J. C.

A Simple Method of Measuring the Affinity between the Solvent and the Dissolved Substance. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 646—647).—If a solvent Y contains in solution the substances X_1, X_2, X_3, . . . X_k, the solutions being of considerable and equal concentrations, and another solvent Z, completely miscible with Y, but practically not dissolving X_1, X_2, X_3, . . . X_k, be added, these substances will be precipitated when sufficient of Z has been added, and the more affinity the dissolved substance bears to Y the more of Z will be necessary. Thus the quantity of Z necessary to completely precipitate X_1, X_2, . . . X_k from unit value of Y solution will be a measure of the affinity X_1, X_2, . . . X_k bears to Y. The method has been applied to the solutions of various salts, etc. Z. K.

Partition Law in Mixed Solvents. II. Walter Herz and Alfred Kurzer (*Zeitsch. Elektrochem.*, 1910, **16**, 869—872).—In addition to the cases previously studied (this vol., ii, 399), the partition of boric acid between water and mixtures of amyl alcohol and carbon disulphide, of iodine between chloroform and mixtures of water and glycerol, of bromine between water and mixtures of carbon tetrachloride and carbon disulphide are investigated. The partition constants for mixtures of two solvents usually differ from the values calculated from the constants of the pure constituents in the sense that the solute is less soluble in the mixture. Two more complicated cases (the partition of picric acid between water and mixtures of chloroform and toluene, and that of iodine between a solution of barium iodide and mixtures of carbon disulphide and carbon tetrachloride) are also examined, and found to follow the same laws which hold for single solvents. The results in the second case indicate the existence of BaI_4 molecules in the aqueous solution. T. E.

Diminution of Velocity of Crystallisation by Addition of Foreign Substances. Herbert Freundlich (*Zeitsch. physikal. Chem.*, 1910, **75**, 245—256).—On the basis of the experimental data of von Pickardt (Abstr., 1903, ii, 66) and of Padoa and Galeati (Abstr., 1904, ii, 714), it is shown that the diminution in the maximum velocity of crystallisation of supercooled liquids due to the addition of foreign substances is represented by the formula $G_0 - G = kc^{1/n}$, where G_0 is the velocity of crystallisation of the fused solvent, G that of the solution, c is the concentration, and k and n are constants; $1/n$ usually lies between 0·2 and 0·7. This can be accounted for on the assumption that the solvent is adsorbed at the crystal faces, and that the diminution in the velocity of crystallisation is proportional to the amount adsorbed (compare Marc, Abstr., 1909, ii, 983). G. S.

Crystallisation of Agar-agar and Gelatin in Connexion with the Mechanism of Gelatinisation. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 653—657).—The author rejects the generally accepted theory that solutions of gelatin, agar-agar, albumin, or other high molecular compounds are disperse systems, liquid + liquid, which are termed emulsoids, and that the gelatinisation of these systems is merely a separation of the two liquids into layers. The solution of such high molecular substances must, on the contrary, be regarded as true solutions, and their gelatinisation as being identical with the process of crystallisation. To obtain emulsoids and suspensoids, a solid substance X is dissolved in a solvent A, and another solvent B, which is miscible in all proportions with A, but does not dissolve X, is added. If the solution is concentrated, the addition of B will at first cause the formation of an emulsion, which will rapidly separate into two layers, X soon crystallising from the layer of A containing it. If a large volume of B is added and the mixture stirred vigorously, X may separate at once. If, however, a fairly dilute solution of X in A is taken, then the addition of B will produce a more stable emulsion and emulsoid, which will only crystallise after very long standing, and the crystals may be microscopic, ultramicroscopic, or even smaller, whilst if the solution is very dilute, the addition of B will at once produce a stable suspension and suspensoid. These considerations have been verified by experiments with manganese sulphate, lithium chromate, potassium carbonate, hydrogen carbonate, and formate, A being water, B an alcohol. With slight modifications, similar experiments with agar-agar and gelatin gave the same results. To obtain a partial precipitation of agar-agar and gelatin, the suspensoid was alternately boiled and cooled, alcohol being added to replace that lost by evaporation. The precipitate thus obtained consisted of very minute, long, crystalline grains rounded at the edges.

Z. K.

Behaviour of Salts of Organic Acids on Melting. Daniel Vörlander (*Ber.*, 1910, **43**, 3120—3135).—In previous papers (Abstr., 1906, i, 317; 1907, ii, 70, 337, 441, 442; 1908, i, 641; ii, 22, 88) attention has been directed to the connexion between the chemical constitution of substances and their power of forming liquid crystals, and in the present paper this investigation is extended, and it is shown that liquid crystals are formed by salts of aliphatic and aromatic acids and by metallic derivatives of phenols, but not by aliphatic hydrocarbons, acids, esters, alcohols, or ketones.

The liquid crystals belong to the same system as those described previously (Abstr., 1908, ii, 88). The salts of the optically active acids are not pleochroic, but certain of them show a play of colours in the liquid crystal state (compare Abstr., 1908, i, 641). The formation of liquid crystals is shown to depend on polarity of structure in the molecule, and their stability and capacity for growing in the direction of the principal axis is due mainly to intramolecular energy difference.

[With R. Wilke and M. E. Huth.]—The sodium and potassium salts of the normal fatty acids from acetic to cerotic were examined,

and it was found that the property of forming liquid crystals begins with butyric acid and ends with stearic, cerotic acid forming "resinous crystals" in the case of the sodium salt, and doubtful "resinous crystals" in that of the potassium salt. A large number of salts with other metals, particularly for the lower acids, were also examined, and details of the behaviour of these on melting are given. Tetramethylammonium stearate forms a liquid crystal phase.

Sodium allylacetate is a good material for the demonstration of liquid crystals, and the sodium salts of undecylenic, elaidic, erucic, and other unsaturated acids also show this phenomenon.

[With M. E. HUTH.]—The tendency to form liquid crystals is greatly influenced by the branching of the chain of carbon atoms, at least among the sodium salts of fatty acids; thus *iso*valeric and *iso*propylacetic acids yield sodium salts, which form liquid crystals, whilst α-methylbutyric and di-α-methylpropionic acids do not, but the potassium salts of all four show this phenomenon.

The alkali salts of the di- and tri-basic fatty acids do not give liquid crystals as a rule.

The alkali salts of the aromatic acids in many cases yield liquid crystals, but no general correlation with constitution can be deduced. Among substituted benzoic acids the salts of ortho-, meta-, and para-derivatives show equal facility in giving liquid crystals, but the ortho-compounds are usually monotropic, whilst the isomeric meta- and para-substances are enantiotropic.

Among phenols, only the potassium derivatives of *o*- and *p*-nitrophenol show the phenomenon.

In carrying out these investigations, great difficulty is experienced in observing the two melting points, and the use of the polarisation microscope with crossed Nicols is unadvisible, owing to the difficulty of observing the temperature. For substances of high melting point, Rinne's heating apparatus, as constructed by Fuess, is used, and for substances of low melting point, a small melting tube with a stirrer of capillary glass tube or a platinum wire. Approximate first and second melting points for a long series of salts of organic acids, thus determined, are given in the original. T. A. H.

Proof of the Movements of Dissolved Molecules Demanded by the Molecular Kinetic Theory. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1910, **74**, 738—742).—In a previous paper (compare this vol., ii, 772) it has been shown that the movements of particles in a colloidal solution is such that the mean deviation from the average number of particles in a definite volume of solution corresponds with that required by the kinetic theory. The same is now proved to be the case for dissolved molecules as a result of experiments with a solution of polonium chloride. A small portion of the solution was covered with a screen coated with zinc sulphide, and the number of α-particles produced in a given time numbered by observing the impacts on the screen in the usual way. When allowance is made for the deviation from the mean owing to the irregular breaking-down of the radioactive atoms, it is found that the momentary differences of

concentration in a limited volume of a true solution correspond with the requirements of the molecular-kinetic theory. G. S.

[History of the Orientation Theory of Matter.] P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide,* 1910, **7**, 256—265).—An historical account is given of the views which have been put forward at different times in reference to the nature of the "amorphous" state. Quotations are given from papers by Fuchs, Frankenheim, and Lehmann. H. M. D.

Coagulation of Colloids. V. A. VOLSCHIN (*J. Russ. Phys. Chem. Soc.,* 1910, **42**, 863—876).—The non-agreement between the numbers obtained by various authors for the coagulating power of the same and analogous coagulating substances is probably due to the various methods employed for obtaining colloidal solutions, the different methods of experiment, and to the varying concentrations of the colloid investigated. To characterise the coagulating power of an ion by a number, it is necessary to investigate: (1) the connexion between the concentration of the coagulating ion and the concentration of the colloid precipitated. (2) Whether this relation is identical or not for ions of different valencies. (3) Whether this relation remains the same for different colloids. The present paper is the first of a series to determine these questions. Soluble Prussian-blue, $Fe_4[Fe(CN)_6]_3$, as obtained directly by the interaction of ferric chloride and potassium ferrocyanide, and the insoluble blue,

$$KFe'''Fe''(CN)_6,$$

in oxalic acid solution were used as colloids, and sodium, potassium and ammonium chlorides as coagulating electrolytes. The main portion of the latter was added from a burette to the colloid of given concentration, and the rest added in very small portions or drop by drop, a small portion of the mixture being withdrawn by a capillary pipette and examined under the microscope after each addition. The commencement of the coagulation could thus be accurately determined. Tables and curves are given showing the number of gram-mols. and concentration of electrolyte necessary to coagulate colloid solution of varying concentration.

The curve for each electrolyte is of exactly the same character, resembling the crystallisation curves in a mixture of two salts. It consists in each case of branches, the breaks coming at exactly the same points on the abscissæ (where are marked the total volume of colloid + electrolyte at coagulation point).

The ordinates (gram-mols. of electrolyte) corresponding with these points are in the ratio:

$$NaCl : NH_4Cl : KCl = 4 : 2 : 1 \text{ for } KFe'''Fe''(CN)_6$$

$$\text{and } NaCl : NH_4Cl : KCl = 1 : \tfrac{1}{3} : \tfrac{1}{4} \text{ for } Fe_4[Fe(CN)_6]_3,$$

and these relations are true whatever the concentration of the colloid. Coagulation by means of electrolytes, although in some respects a purely physical phenomena, may yet exhibit laws characteristic of purely chemical processes, and this is particularly the case with the substances dealt with here. Z. K.

Filtration of Colloidal Solutions. A New Filter. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1910, **24**, 354—367).—The addition of a certain quantity of glycerol to an ethereal-alcoholic solution of cellulose nitrate increases the permeability of the collodion membrane made from such solutions. The membrane, however, is not stable on exposure to the air, as it contracts and glycerol is exuded. If castor oil is added as well as glycerol, a stable membrane is obtained, which does not contract on exposure to the air, and can be preserved for a long time between filter paper in order to keep away moisture. It can be used as an ultra-filter, which works under the pressure of the liquid contained in it, no extra pressure being necessary. To prepare it for use, it is simply soaked in water to dissolve out the glycerol. The solutions which gave the best membranes contained four parts of cellulose nitrate, 3·5 parts of castor oil, and 2·5, 3, 4, and 5 parts respectively of glycerol, the alcohol and ether used to form the solution being in the proportion 10 parts of alcohol to 80 parts of ether.

Experiments on the filtration of colloidal solutions, classified according to the size of the particles (compare Bechhold, Abstr., 1908, ii, 24, 823), showed that the smaller the particles, the smaller is the amount of glycerol which should be used to obtain membranes which will retain the particles.

The membranes so made can only be used for the filtration of colloidal solutions containing particles varying in size from those of colloidal arsenic sulphide to colloidal Prussian-blue (compare Bechhold, *loc. cit.*). The author has succeeded in separating colloidal arsenic sulphide from Prussian-blue by filtration through the membrane containing 4 parts of glycerol to 4 and 3·5 parts of cellulose nitrate and castor oil respectively. T. S. P.

The Action of Chloroform on Lipoid Suspensions. D. CALUGAREANU (*Biochem. Zeitsch.*, 1910, **29**, 96—101).—The appearances are described when cholesterol and other lipoids in colloidal solution are shaken with chloroform and other solvents which are not miscible with water. The particles of the lipoid increase in size, and in the case of cholesterol lose their crystalline form, and form a kind of precipitate on the surface of the chloroform when this solvent is employed in the experiment. The phenomenon is ascribed to the adsorption of the chloroform on the surface of the lipoid, and is contrasted with the phenomena observed when colloidal metals, such as gold and silver. are shaken with mercury. Here no adsorption takes place, and the difference of action is ascribed to the fact that the mercury, in contrast to chloroform, is not soluble in water.

S. B. S.

The System Chlorine–Sulphur Dioxide. ANDREAS SMITS and W. J. DE MOOY (*Proc. K. Akad. Wetensch. Amsterdam*, 1910. **13**, 339—341).—The nature of this system has been investigated by freezing-point measurements. The melting points of chlorine and sulphur dioxide are $-100·45°$ and $-75·6°$ respectively. The data obtained in the dark indicate a eutectic point at $-102·3°$, the

composition corresponding with 1·5 mols. % of sulphur dioxide. From the form of the freezing-point curve, the authors conclude that mixed crystals are formed.

Measurements in which the mixtures were subjected to sunlight or the light from a quartz mercury lamp show that sulphuryl chloride is formed very rapidly in these circumstances. A mixture containing 47·1 mols. % of sulphur dioxide, in which equilibrium had been established in sunlight, was found to exhibit initial solidification at $-80°$, which is very much higher than the temperature corresponding with the freezing-point curve for the system in the dark.

H. M. D.

Critical End-Points in Ternary Systems. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 342—352).—The gradual changes which the critical solution phenomena exhibit when a third substance is added to a binary system are discussed. The third substance is of such a nature that it does not yield critical end-points with either of the components of the binary system, and is completely miscible with these components in the liquid state. The binary system to which special reference is made is that of ethyl ether–anthraquinone, which has been previously examined in detail, and the third substance is ethyl alcohol.

H. M. D.

Critical Phenomena of the Ternary System Ethyl Ether, Anthraquinone, and Naphthalene. ADA PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 353—359).—Experiments have been made to ascertain the nature of the critical solution phenomena which are exhibited when the binary system ethyl ether–anthraquinone is converted into a ternary system by the addition of naphthalene. For small quantities of naphthalene the two critical end-points, which are characteristic of the binary system, are still observable. As the proportion of naphthalene increases, the end-points approximate to one another, and the spacial region bounded by the critical curves disappears as a result of this approximation when the proportion of naphthalene added amounts to 4·5%.

H. M. D.

The Ternary Systems Alkali–Phosphoric Acid–Water. JOH. D'ANS and O. SCHREINER (*Zeitsch. physikal. Chem.*, 1910, **75**, 95—107). —The equilibria in these systems have been determined by solubility measurements at 25° in the usual way, and the results are given in tabular form, and also represented graphically.

In the system containing sodium salts, the solid phases met with were the compounds $Na_3PO_4,12H_2O$, $Na_2HPO_4,12H_2O$, $Na_2HPO_4,7H_2O$, $NaH_2PO_4,2H_2O$. Trisodium phosphate dodecahydrate has a transition temperature at $70·75 \pm 0·1°$. The corresponding disodium salt has two transition points, the first, represented by the equation $Na_2HPO_4,12H_2O \rightleftharpoons Na_2HPO_4,7H_2O + 5H_2O$, at $35·4 \pm 0·05°$; the second, $Na_2HPO_4,7H_2O \rightleftharpoons Na_2HPO_4,2H_2O + 5H_2O$, at $48·35 \pm 0·05°$. The solubility, in grams anhydrous salt per 100 grams of water, is 46·11 at the former, and 79·00 at the latter, transition point. The region of the acid mono-

sodium phosphate described by previous observers was not reached; it is stable only in the presence of practically pure phosphoric acid.

In the system containing potassium salts, only the three anhydrous salts, K_3PO_4, K_2HPO_4, and KH_2PO_4 were met with. The investigation was difficult owing to the extremely high solubility of the di- and tri-potassium salts. The region within which K_2HPO_4 exists is very narrow, lying between the ratios $K : PO_4 = 6{\cdot}9 : 4{\cdot}15$ and $K : PO_4 = 4{\cdot}8 : 3$ or $K : PO_4 = 1{\cdot}66 : 1{\cdot}60$. The region of the acid monosodium phosphate, KH_2PO_4,H_3PO_4, described in the literature was not reached.

In the system containing ammonium salts, the compounds

$$(NH_4)_3PO_4,3H_2O,\ (NH_4)_2HPO_4,\ \text{and}\ NH_4{\cdot}H_2PO_4,$$

were met with as solid phases. The diammonium salt exists only within narrow limits of concentration.

For all three alkalis, the systems in which the solution and the solid phase have the ratio PO_4 : alkali = 1 : 1 represent an absolute minimum in the solubility of these compounds; in other words, the solubility of the monoalkali phosphates is increased by the addition of alkali as well as of phosphoric acid. G. S.

Stability of the Two Crystalline Modifications of Phenol. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1910, **75**, 75—80).—The conditions of stability of the different forms of phenol have been further investigated (compare Abstr., 1909, ii, 983) by an improved experimental method.

As a preliminary to the preparation of phenol II (the denser modification) in open vessels at atmospheric pressure, curves are plotted giving the temperatures and corresponding pressures at which the velocity of transformation of phenol II to phenol I in the presence of both phases becomes appreciable. Further, the conditions under which spontaneous transformation of phenol II to phenol I (ordinary phenol) takes place are tabulated. At $-39°$, the latter change takes place at 154 kilog./cm.^{2} pressure; at $-28{\cdot}2°$, 410 kilog.; at $+3{\cdot}5°$, 1025 kilog., and at 29°, 1625 kilog. At $-80°$, no appreciable change takes place in a considerable time at atmospheric pressure.

Phenol II was prepared at 15° under a pressure of 3000 kilog./cm.^{2}. The cylinder of nickel steel containing it was then cooled at $-80°$, and the pressure gradually lowered to 1 kilog. After some further manipulations, phenol II was obtained, and freed from its wrappings in a mixture of light petroleum and chloroform cooled to $-80°$, in which it sank, whereas a piece of ordinary phenol floated in the mixture. The diminution of volume when phenol I changes to phenol II is 0·06 cm. per gram. G. S.

[Temperature-coefficient of Chemical Reaction Velocities.] Correction. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1910, **74**, 747).—A correction is applied to one of the author's formulæ on this subject (compare this vol., ii, 24) which simplifies it and renders it more accessible to experimental investigation. G. S.

Slow Combustion of Sulphur. MAX BODENSTEIN and WALTER KARO (*Zeitsch. physikal. Chem.*, 1910, **75**, 30—47).—Ewan (Abstr., 1895, ii, 213) found that the rate of oxidation of sulphur is proportional to

the square root of the pressure of the oxygen, but the present authors have obtained entirely different results.

The sulphur was heated at constant temperature (252°) with oxygen in a glass tube for definite intervals, the mixture of oxygen and sulphur dioxide transferred to a measuring vessel, and the proportion of sulphur dioxide in the mixture determined by observation of the pressure before and after absorption of the sulphur dioxide with an iodine–potassium iodide solution.

The rate of reaction is directly proportional to the pressure of the oxygen, and is roughly proportional to the surface of the sulphur. The rate increases in the ratio 1·87 : 1 for a rise of temperature of 10°. From these observations the conclusion is drawn that the controlling reaction is a chemical one, which takes place in the adsorption layer on the surface of the sulphur. The excellent agreement of the velocity-coefficients shows that the sulphur dioxide, which must accumulate in the adsorption layer, has no influence on the reaction velocity, and the authors show that this can be reconciled with their view as to the mechanism of the reaction.

At 159°, the temperature at which Ewan worked, the rate of oxidation of sulphur is extremely slow, and this observer must therefore have measured some other reaction. His heated sulphur was near a soda-lime tube (used for absorbing the sulphur dioxide), and it is suggested that the sulphur distilled over to the soda-lime, forming polysulphides and thiosulphate, which were very rapidly oxidised by the oxygen. G. S.

Specific Stereochemical Behaviour of Catalysts. KASIMIR FAJANO (*Zeitsch. physikal. Chem.*, 1910, **75**, 232—234. Compare this vol., ii, 599).—The point at issue between the author and Rosenthaler (this vol., ii, 232) requires further experimental investigation. G. S.

Dead Spaces. RAPHAEL ED. LIESEGANG (*Zeitsch. angew. Chem.*, 1910, **23**, 2124—2125).—A small glass tube, open at both ends and filled with a 10% jelly containing sodium chloride, is immersed in a solution of silver nitrate. When the diffusion of the silver nitrate and the precipitation of silver chloride is complete, a clear space of several mm. is left in the centre of the tube, where no precipitation has occurred. It contains silver nitrate but no chloride. This "dead space" is due to the fact that the sodium chloride has diffused away to the places where precipitation of silver chloride has occurred. Such a "dead space" is not formed when the substance dissolved in the jelly is not diffusible, for example, when the jelly contains albumin and the tube is immersed in metaphosphoric acid.

If the jelly contains potassium dichromate instead of sodium chloride, a "dead space" is still formed in the middle of the tube. The silver chromate deposit is not continuous, however, as in the case of silver chloride, but in the form of rings with clear spaces between (the ordinary Liesegang phenomenon). The latter clear spaces are not identical with the "dead space" in the centre of the tube, if a "dead space" is defined as one where no chemical reaction has taken place,

since silver chromate has been formed in them, and while in supersaturated solution has diffused to the places where precipitation has taken place. These results make it doubtful whether the phenomena observed by Liebreich (Abstr., 1891, 1150) are really due to the occurrence of "dead spaces."

The importance of these phenomena in connexion with, for example, the occurrence in many bones of zones poor in lime is pointed out.

T. S. P.

Repeating Figures in the Atomic Weight Values. F. H. LORING (*Chem. News*, 1910, **102**, 228—229).—In the International Tables for 1911 there appears to be a tendency for the figure in the unit's place to recur in the second place of the decimals, for example, Ag = 107·87, Fe = 55·85, but this may be accidental. G. S.

A New Valve. AUG. KUMM (*Chem. Zeit.*, 1910, **34**, 1136).—A valve for preventing the return of water into vessels while being exhausted by the filter-pump is described. A glass rod is supported on the mouth of a vertical glass tube by means of an expansion covered with indiarubber. During suction the valve is raised, but if the pump is stopped, or if water returns, the rubber-covered expansion makes a tight joint with the tube. C. H. D.

Modified Drying Tube. EDWIN DOWZARD (*Amer. J. Pharm.*, 1910, **82**, 509—510).—By inserting a stopcock in the lower part of a Pelligot drying tube, the exhausted sulphuric acid may be removed and replaced with fresh acid by suction at the side-tube without dismounting connected apparatus. A small test-tube is suspended under the stopcock to catch drops of exuding acid. T. A. H.

Extraction Apparatus. R. P. NOBLE (*J. Amer. Chem. Soc.*, 1910, **32**, 1533).—A form of apparatus for the extraction of substances by means of mixed solvents is described. It consists of a glass tube, the bottom of which is connected with a syphon tube, to the upper end of which a side-tube is attached. The substance to be extracted is contained in a cartridge, and the solvent is removed by actuating the syphon. The apparatus avoids the use of any stopcock.

H. M. D.

Lecture and Laboratory Apparatus. JAMES A. SCHOFIELD (*Austral. Assoc. Report*, 1909, 167—172).—The following forms of apparatus are described. I. Apparatus for showing the composition of nitrous and nitric oxides. Instead of the original method devised by Davy for heating sodium in the gas, the sodium is contained in a deflagrating spoon and fired electrically. The gas is confined in one limb of a manometer, the electrical connexions passing through a rubber cork at the top of the tube. II. Apparatus for the preparation of ammonium hydroxide solution, concentrated and dilute, from liquid ammonia. III. A rapid form of condenser for distilled water. The condenser is practically a reversed tubular boiler, nine $\frac{1}{2}$-in. tin tubes 1 ft. long forming the condenser. IV. A cheap demonstration balance. Fitted to the centre of the beam, and projecting above it, is a light aluminium

pointer, about 21 inches long, playing over a cardboard scale. This scale and pointer are turned towards the class, the ordinary scale and pointer being towards the lecturer. The aluminium pointer is counterbalanced by a binding screw clamped on to the ordinary pointer. V. Nickel crucibles for the Laurence Smith method of determining alkalis in silicates. These crucibles are used for the decomposition of silicates with calcium carbonate and ammonium chloride, and give the same results as platinum ones. T. S. P.

Apparatus for Laboratories and Lecture Experiments. JOHANNES THIELE (*Annalen*, 1910, **376**, 279—285).—Chlorinations and brominations, and also the detection of feeble fluorescence, can be accomplished very successfully in the light of an arc lamp instead of in sunlight. Apparatus for the demonstration of the production of water in quantity from its elements and of the combustion of nitrogen are described, and also electrically heated filter funnels, boiling-point apparatus, etc.

Many lecture experiments, in which the reagents are heated to boiling, can be performed in very much shorter time by placing a little of the not too dilute reagents in an upright cylinder and adding much boiling water. The hydrolysis of ferric alum, the formation and decomposition of copper hydride, the hydrolysis of carbonates and of sucrose, the decomposition of mercuric nitrate, and the hydrolysis of ferric chloride are thus readily demonstrated. C. S.

Inorganic Chemistry.

Preparation of Pure Hydrogen Peroxide for Medical Purposes. OTTO SCHMATOLLA (*Pharm. Zeit.*, 1910, **55**, 888—889).—The method used consists essentially of (1) solution of commercial barium peroxide in hydrochloric acid, phosphoric acid being added to precipitate metals such as iron; (2) precipitation from the solution of hydrated barium peroxide by means of sodium hydroxide; and (3) preparation of the solution of hydrogen peroxide in the usual way by the addition of the hydrated barium peroxide to sulphuric acid.

T. S. P.

Formation of Hydrogen Peroxide. K. V. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 900—904).—Papers prepared with cobalt naphthenate are very sensitive to hydrogen peroxide, turning from pink to olive-green (compare this vol., ii, 238). In bright sunlight or by a rise of temperature they become still more sensitive, it being possible to detect one part in 1,000,000 of water.

Water containing oxygen when exposed to bright sunlight gives the hydrogen peroxide reaction after the following intervals: at 9—22°, after twelve days; 19—31°, after eight days; 20—41°, after seven days.

If the oxygen is replaced by air, no hydrogen peroxide is formed. In similar experiments with radioactive barium chloride, and also the nitrates of barium, lead, thorium, uranium, and bismuth, hydrogen peroxide was formed only in the presence of radioactive barium salt and of lead nitrate. When, however, the experiment was made in the dark, even radioactive barium produced a negative result; it is therefore considered that it is not the radium emanation which induces the reaction $2H_2O = H_2O_2 + H_2$, but that the radium salt acts as a catalyst.

Hydrogen peroxide is also formed on the surface of moist, porous substances, such as wood, asbestos, and so forth. Z. K.

Formation of Hydrogen Peroxide in the Combustion of Detonating Gas. K. V. CHARITSCHKOFF and AMBARDANOFF (*J. Russ. Phys. Chem. Soc*, 1910, **42**, 904).—Using the cobalt naphthenate papers (compare preceding abstract), hydrogen peroxide was detected in the products of combustion of detonating gas, 0·000476 c.c. hydrogen peroxide being produced from the combustion of about 25 litres of hydrogen in oxygen.

Hydrogen peroxide could not be detected in the combustion of benzene or of alcohol. Z. K.

Colour of Iodine Solutions. JOEL H. HILDEBRAND (*Zeitsch. physikal. Chem.*, 1910, **74**, 679—682).—The author answers some adverse criticisms of Waentig (this vol., ii, 117) on his and Glascock's work on this subject (compare Abstr., 1909, ii, 225). In particular, the standard solution (for comparison purposes) was prepared by adding to the violet solution of known iodine concentration sufficient of the "active" solvent to be investigated to change the violet colour completely to brown, so that Waentig's objection that the authors had assumed the colour of the additive compound to be the same for all the solvents used is not valid. G. S.

Solubility of "Insoluble" Sulphur ($S\mu$). ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1910, **75**, 235—244. Compare Abstr., 1910, ii, 228).—When amorphous insoluble sulphur, $S\mu$, is treated with carbon disulphide or carbon tetrachloride, a small proportion of it (usually not exceeding 3 per cent. with carbon disulphide) goes into solution, the proportion depending on the time of action, the temperature, and the nature of the solvent, but being independent of the amount of solvent. This is ascribed to a partial change of $S\mu$ to soluble sulphur, $S\lambda$, under the influence of the solvent. Further, a small amount of $S\mu$, under ordinary conditions less than 1 in 1000, goes into solution unaltered, probably in the colloidal form.

The author maintains the accuracy of his figure, 118·95, for the melting point of monoclinic sulphur. G. S.

The Supposed Nitrososulphonic Acid of Raschig (Sabatier's Nitrosodisulphonic Acid) and the Theory of the Lead Chamber Process. WILHELM MANCHOT (*Zeitsch. angew. Chem.*, 1910, **23**, 2113—2114).—Raschig's theory of the lead chamber

process assumes the intermediate formation of nitrososulphonic acid, $HO{\cdot}NO{\cdot}SO_3H$ (compare Abstr., 1908, ii, 30), the solution of which in concentrated sulphuric acid has a blue colour; in more dilute acids there is a slight red colour. This blue colour is also produced by the action of a mixture of sodium nitrite and mercury on sulphuric acid, but disappears after a time, nitric oxide being evolved.

The author finds that the solution of nitric oxide in pure sulphuric acid is colourless; if, however, the sulphuric acid contains iron, a red coloration is produced. The red coloration observed by Raschig in some experiments of his (Abstr., 1905, ii, 23, 700), and also a solubility of nitric oxide in sulphuric acid considerably greater than that observed by the author, are due to the use of impure sulphuric acid. The "purple acid" from the Gay Lussac tower is nothing more than a solution of the ferrous or ferric sulphate compound of nitric oxide.

The brown coloration produced by the solution of nitric oxide in an aqueous solution of ferrous sulphate is not due to the formation of ferrous nitrososulphonate, $ON{<}{}^{-O-}_{SO_3}{>}Fe$, as assumed by Raschig, since the same colour is produced with ferrous chloride and ferrous hydroxide. The compounds formed contain one molecule of nitric oxide to one atom of iron, and are probably of the type $NO{\cdot}FeCl_2$ (compare Abstr., 1907, ii, 93). For similar reasons it is probable that Raschig's copper nitrososulphonate does not exist (compare this vol., ii, 956).

Thus the existence of a nitrososulphonic acid has still to be proved. The same objections may also be raised to Sabatier's nitrosodisulphonic acid. T. S. P.

Revision of the Atomic Weight of Nitrogen. Exact Analysis of Nitrogen Tetroxide. PHILIPPE A. GUYE and G. DROUGININE (*J. Chim. Phys.*, 1910, 8, 473—514).—The atomic weight of nitrogen has been determined by decomposing weighed quantities of nitrogen tetroxide with incandescent iron wire.

The possibility of obtaining pure nitrogen tetroxide for the purpose depends on the following considerations. Nitrogen trioxide is easily oxidised at the ordinary temperature to tetroxide. The tetroxide is not further attacked by oxygen, although it is oxidised by ozone; on the contrary, the pentoxide undergoes spontaneous decomposition into tetroxide and oxygen. The equilibrium between nitrogen tetroxide and nitric oxide plus oxygen has been determined, and the result shows that the dissociation of tetroxide is negligible under the conditions of experiment. The calculations are not affected by the question as to whether the formula of the tetroxide is NO_2 or N_2O_4. The vapour-pressure curves of nitric oxide, nitrogen tetroxide, and nitrogen trioxide (prepared by Baker's method) were determined in an apparatus specially designed to protect the surface of the mercury by a buffer of air from corrosion by the tetroxide. The curves, which are in accord with those of Ramsay and Young, indicate that although the tetroxide should be easily separated from nitric oxide by distillation, the removal of trioxide would be difficult. Accordingly, the tetroxide was prepared by mixing purified and carefully dried nitric oxide with

excess of purified oxygen, and was distilled in a vacuum at least ten times in presence of free oxygen, precautions being taken to free the final product from dissolved oxygen. The absence of traces of trioxide was inferred from the colourless nature of the liquid product. Throughout the mainpulations, phosphoric oxide was used to exclude moisture.

The decomposition apparatus consisted of an oval bulb placed with its major axis horizontal, and provided with a stopcock at the top and a tubulure for condensing the gas at the bottom. A spiral of iron wire which traversed the bulb could be heated electrically. It was prepared for use by alternate oxidation and reduction in a low pressure current of dry hydrogen.

From one to two grams of dry nitrogen tetroxide of f. p. $-9\cdot6°$ were distilled into the bulb, and solidified in the tubulure by a freezing mixture. The bulb, having been evacuated and closed, was allowed to warm up, and weighed. After passing the current and removing the residual nitrogen by the pump, the bulb was weighed again.

The mean of seven determinations gives 14·010 as the atomic weight of nitrogen, or neglecting the two first determinations, the remaining five give a mean value 14·009 ($O=16$). Considering the possible sources of error, the atomic weight could not be less than 14·005, and probably not less than 14·008.

The values obtained are in good agreement with those deduced from analyses of nitrous oxide by Guye (14·0107) and analyses of nitric oxide by Gray (14·0097), but are opposed to those recently calculated by Richards from analyses of silver nitrate, namely, 13·990 to 14·002. The authors consider that the various direct measurements of nitrogen-oxygen ratios are more trustworthy and agree better amongst themselves than the indirect (silver) values, and that it would be reasonable to make the atomic weight of silver depend on the directly determined value for nitrogen, since this is supported by the physical constants of nitrogen. R. J. C.

Formation of Nitric Oxide in the High Tension Arc. FRITZ HABER, ADOLF KOENIG, and E. PLATOU (*Zeitsch. Elektrochem.*, 1910, **16**, 789—796).—The apparatus and method of experiment have been described in previous papers (Abstr., 1908, ii, 34, 940). Two sets of experiments were made. In the first set, the length of arc and the current (0·27 ampere) were kept constant, and the pressure of the air varied. The results show a very decided maximum yield at 150 mm., the gas leaving the arc containing 8·16% of nitric oxide at this pressure. The second set was designed to determine the relationship between the energy consumed in the arc and the quantity of nitric oxide produced. Owing to the distortion of the voltage curve by the discharge through the gas, the curves of voltage and current are not in the same phase, which introduces some difficulty in the measurement of the energy used in the arc. The methods of measurement are described in detail. The best yield in twenty-four experiments with air at 140 mm. pressure was 57 grams of nitric acid per kilowatt-hour, with 3·4% of nitric oxide in the gas leaving the arc. T. E.

Formation of Nitric Oxide from Air by means of High Frequency, Alternating, Electrical Discharges. FRITZ HABER and E. PLATOU (*Zeitsch. Elektrochem.*, 1910, **16**, 796—803).—The electrical measurement of the energy consumed in an unsteady arc produced by an high frequency, alternating current is impossible. The authors have, therefore, measured it by immersing the apparatus in which the discharge occurs in a calorimeter consisting of a Dewar's tube filled with paraffin oil. The platinum resistance thermometer also serves as a stirrer, and the hot gases leave the discharge tube through a silver tube filled with silver filings, which is immersed in the oil and serves to cool them. The discharge takes place between platinum wires placed closed together at their lower extremities and diverging at their upper ends. Good results are only obtained when considerable quantities of energy are used in the arc, and when it is well spread out in a fan-shape. With a current of about 500 periods per second, and air at atmospheric pressure, the yield is as high as 54 grams of nitric oxide per kilowatt-hour; with about one hundred times higher frequency, slightly worse results were obtained (48·7 grams of nitric acid per kilowatt-hour), whilst diminishing the pressure to 387 mm. reduced the yield to about 20 grams. The lower yields are, however, ascribed to the tendency of the arc to hang to one spot on the platinum wires instead of travelling along them, and the authors think that neither pressure nor frequency have any specific influence on the yield obtainable. T. E.

Yield of Nitric Oxide in the Combustion of Air in the Cooled, Direct-current Arc. WILHELM HOLWECH and ADOLF KOENIG (*Zeitsch. Elektrochem.*, 1910, **16**, 803—810).—An iron wire, 2 mm. diameter, surrounded by a quartz tube served as cathode. The anodes were water-cooled, copper capillary tubes of from 0·5 to 3 mm. bore. The electrodes were usually placed 2 to 5 mm. apart, and the air was drawn off through the capillary tube by means of an air pump; the arc is thus drawn into the cold capillary tube, and the greater part of its length, which varies with the rate at which the air flows, is within the tube. The cathode was not heated as in Holwech's experiments with the same arrangement (this vol., ii, 578), but this had no effect on the results. The yields are always better when the capillary anode is vertically below the cathode, and the air, therefore, drawn downwards, than it is when their positions are reversed. The yield increases with the velocity of the air current (the percentage of nitric oxide in the gas, of course, decreases); with the 0·5 mm. capillary a yield of 74·3 grams of nitric acid per kilowatt-hour was obtained, using air, with 1·94% of nitric oxide in the gas, the arc taking 0·29 ampere at 290 volts. The best results were obtained with the 2 mm. capillary tube, 84·8 grams of nitric acid per kilowatt hour being reached with 2·3% of nitric oxide in the gas, a current of 0·2 ampere, and 280 volts. Attempts to concentrate more energy into the arc gave worse results; reversing the poles and using alternating current also were less successful. T. E.

Formation of Nitric Oxide from Air in the Arc under Pressure. FRITZ HABER and WILHELM HOLWECH. (*Zeitsch. Elektrochem.*, 1910, **16**, 810—813).—The arc is formed in a vertical steel tube between a cooled copper cathode and an iron anode placed respectively at the top and bottom of the tube. The air is blown in at the bottom tangentially to the walls of the tube. In one arrangement, cold air was used, in another it was heated by passing over the outside of the steel tube before entering it. With the first arrangement, 0·55 to 1·5 ampere at 700 to 2075 volts were used, and pressures varying from 2 to 21 atmospheres. The best yield was 76 grams of nitric acid per kilowatt-hour with 2 atmos. pressure and 0·36% of nitric oxide. The same yield was obtained at 11 atmos. with only 0·29% of nitric oxide in the gas. With pre-heated air, using currents of 0·5 to 0·6 ampere and 1200 to 1460 volts, the yields were better, 82·8 grams of nitric acid per kilowatt-hour being obtained with 4 atmos. pressure and 0·76% of nitric oxide. At higher pressures, the yields were rather lower. T. E.

Formation of Nitric Oxide during the Combustion of Hydrogen. A. WOLOKITIN (*Zeitsch. Elektrochem.*, 1910, **16**, 814—826).—The experiments of Haber and Coates (Abstr., 1909, ii, 997) on the formation of nitric oxide during the combustion of carbon monoxide in mixtures of oxygen and nitrogen are extended to hydrogen, using the same apparatus and methods of experiment. The results are very similar; the combustion of hydrogen in air at the ordinary pressure yields no nitric oxide; when the pressure is increased to 20 atmospheres or more, about 0·3 mol. of nitric oxide is formed per 100 mols. of water. With a mixture of equal volumes of oxygen and nitrogen, the yield is small at low pressures, but increases with the pressure, nearly 3 mols. of nitric oxide per 100 mols. of water being obtained at 15 atmos. pressure. Further increase of the pressure up to 50 atmos. produces but little further increase in the yield. A mixture of oxygen and nitrogen with 80% of the former behaves in much the same way as the mixture of equal volumes. The theoretical calculation of the yield, made in the manner adopted by Haber and Coates, indicates a maximum yield of about 4 mols. of nitric oxide per 100 mols. of water, using a mixture of equal volumes of oxygen and nitrogen; the actual yields are less than the theoretical ones, whereas Haber and Coates obtained the opposite result with carbon monoxide. T. E.

The Behaviour of Nitrous Gases towards Water and Aqueous Alkalis. FRITZ FOERSTER and J. BLICH (*Zeitsch. angew. Chem.*, 1910, **23**, 2017—2025. Compare Abstr., 1908, ii, 941, 1031). —The rate of oxidation of nitric oxide by air under different conditions has been determined by absorbing the product in sodium hydroxide and determining the ratio of nitrite to nitrate formed.

In the authors' apparatus, the gases issuing from the large oxidation chamber pass through two vessels containing water, after which the mixture contains nitric oxide as well as peroxide. The third vessel

contains sodium hydroxide. Lengthening the path between the water and alkali increases the completeness of the oxidation, but no improvement is brought about by interposing heated glass spirals. Experiments in which air and nitric oxide pass together into a heated vessel containing broken glass show that the reaction $2NO + O_2 = 2NO_2$ proceeds less rapidly as the temperature rises. This result has also been observed by Bodenstein, and is best explained by the assumption that a molecular oxide is first formed: $NO + O_2 \longrightarrow NO{\cdot}O_2$, $NO{\cdot}O_2 + NO \longrightarrow 2NO_2$ (compare Raschig, Abstr., 1907, ii, 455).

The experiments also show that alkalis absorb nitrogen trioxide more rapidly than nitrogen peroxide. It appears probable that in a partly oxidised mixture the equilibrium $NO + NO_2 \rightleftarrows N_2O_3$ exists, although the quantity of trioxide is small, and that the water absorbs the gases in this form (compare Le Blanc, *Zeitsch. Elektrochem.*, 1906, **12**, 544). When pure liquid nitrogen trioxide is added to sodium hydroxide solution at $-22°$, it is instantly absorbed, whilst liquid nitrogen peroxide only reacts slowly. C. H. D.

The Reduction of Nitrosyl Chloride. HUMPHREY O. JONES and J. K. MATHEWS (*Proc. Camb. Phil. Soc.*, 1910, **15**, 529—530).—When nitrosyl chloride and ethyl mercaptan react in ethereal solution at $-80°$, small quantities of hydroxylamine hydrochloride are formed. The action of other reducing agents on nitrosyl chloride has therefore been studied, but the formation of hydroxylamine hydrochloride has only been observed when nitrosyl chloride and hydrogen are passed over reduced platinum, cooled in a freezing mixture. Even in this case the hydroxylamine hydrochloride only forms 5% of the ammonium chloride produced. When the contact substance is nickel, the product is ammonium chloride.

With palladium, the products at the ordinary temperature are palladium chloride, nitric oxide, and nitrogen; at higher temperatures ammonium chloride is formed.

Hydrogen sulphide and nitrosyl chloride interact at a low temperature in ether or light petroleum, the principal reaction being

$$NOCl + 3H_2S = NH_4Cl + H_2O + 3S.$$

C. H. D.

Presence of a Small Quantity of Carbon Monoxide in the Atmosphere of Coal Mines. P. MAHLER and J. DENET (*Compt. rend.*, 1910, **151**, 645—647. Compare this vol., ii, 607; Boudouard, Abstr., 1909, ii, 234).—Carbon monoxide has been found to occur in the air of well-ventilated coal mines to the extent of about 0·002% by volume; the maximum amount found was 0·004%. Iodic anhydride was employed to estimate the carbon monoxide, and precautions were taken to avoid the influence of traces of dust or unsaturated hydrocarbons. W. O. W.

Silicates with Linked Silicon Atoms. WILHELM MANCHOT (*Ber.*, 1910, **43**, 2603—2604).—In his lecture before the German Chemical Society (this vol., ii, 780), W. Pukall represents the constitution of "kaolin-acid" as $\begin{array}{l} OH{\cdot}Si{\cdot}O{\cdot}O{\cdot}Al(OH)_2 \\ \quad \| \\ OH{\cdot}Si{\cdot}O{\cdot}O{\cdot}Al(OH)_2 \end{array}$, there being a double linking

between the two atoms of silicon. A similar constitution is given to kaolin.

The author points out that such substances should evolve hydrogen when treated with hydrofluoric acid, or with hydrofluoric acid followed by alkali (compare Abstr., 1905, ii, 165; 1908, ii, 46), and that therefore the above formula is an impossible one. Moreover, the doubly linked atoms of silicon would indicate that a reduction of silicic acid had taken place in the preparation of the compound, whereas no reduction could take place according to the method of preparation described by Pukall. Such a linking would be broken by the action of alkali and not be stable, as postulated by Pukall.

T. S. P.

Preparation of Argon. GEORGES CLAUDE (*Compt. rend.*, 1910, **151**, 752—753).—Details are given of a laboratory method for preparing argon at the rate of 2—3 litres per hour. The compressed oxygen of commerce, when obtained from liquid air, contains over 3% of argon, and is a convenient source of this element. The oxygen is absorbed by reduced copper, and the small amount of nitrogen by heated magnesium. W. O. W.

Determination of the Velocity of Sound in Potassium Vapour and the Monatomicity of its Molecules. WILHELM WENZ (*Ann. Physik.*, 1910, [iv], **33**, 951—970).—Measurements of the velocity of sound in potassium vapour have been made by Quincke's resonance method at 850°. The vapour was contained in a steel tube surrounded by a wider porcelain tube, which was heated electrically. The one end of the steel tube was closed by a thin mica plate serving as a vibrating resonance diaphragm. In order to obtain satisfactory results with this at the high temperature, it was found necessary to protect the inner surface with a thin layer of silver. The other end of the tube was formed by a piston which could be moved up and down, and by this means the length of the column of vapour could be varied. The distances between successive positions in which resonant vibration was obtained were determined, and compared with the corresponding lengths for air. The measurements give 1·77 for the ratio of the specific heats. From this, the author concludes that the vapour of potassium consists of monatomic molecules. H. M. D.

Equilibrium in the System: Potassium Iodide, Iodine, and Aqueous Alcohol. CHARLES L. PARSONS and H. P. CORLISS (*J. Amer. Chem. Soc.*, 1910, **32**, 1367—1378).—The solubility of iodine and potassium iodide in aqueous-alcoholic solutions containing varying amounts of potassium iodide and iodine respectively has been measured at 25°. In an alcohol-water mixture containing 60% of alcohol, two solubility curves are obtained, which intersect at a point corresponding with a solution containing 20·0% of potassium iodide and 72·5% of iodine. Similar results were obtained with a solvent containing 40% of alcohol, the point of intersection of the two curves corresponding in this case with 22·5% of potassium iodide and 70·8% of iodine. The limiting solutions

indicated are those which are simultaneously saturated with respect to iodine and potassium iodide. The solubility data afford no evidence of the formation of solid polyiodides, and the absence of these has been confirmed by analyses of the solid phases in contact with the saturated solutions.

The question of the existence of polyiodides in solution is discussed and experiments are described which show that the iodine and potassium iodide in an aqueous solution of these substances can be partly separated by diffusion. These results are interpreted as indicating that polyiodides are not formed to any appreciable extent. The increased solubility of iodine in an iodide solution as compared with pure water is attributed to the high solvent power of the dissolved solid. H. M. D.

Sodium Tellurides. GIOVANNI PELLINI and E. QUERCIGH (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 350—356. Compare Tibbals, Abstr., 1909, ii, 728).—With a view to throwing further light on the analogy between tellurium, sulphur, and selenium, the authors have investigated the sodium tellurides by thermal methods. The cooling curves of mixtures of the two elements were observed in an atmosphere of nitrogen, a quartz vessel being employed, and the temperatures measured by means of a platinum and platinum-rhodium couple. The results obtained are also exhibited in a curve, from which it follows that under the conditions of the experiment three compounds can exist, namely, Na_2Te, Na_3Te_2, Na_3Te_7. Only the first melts unchanged. It is whitish in colour, but rapidly darkens in the air, and is very deliquescent. The other two have a grey, metallic aspect. In these circumstances it was not possible to obtain the compound Na_2Te_3 prepared by Tibbals (*loc. cit.*). The formulæ of these tellurides differ from those of the selenides (compare Mathewson, Abstr., 1907, ii, 682) and sulphides, except in the case of the type Na_2Te. R. V. S.

The Equilibrium Diagram of the Silver–Sodium Alloys. E. QUERCIGH (*Zeitsch. anorg. Chem.*, 1910, **68**, 301—306).—Sodium does not react appreciably with silver below 700°. The alloys may be prepared in all proportions by fusion in a current of nitrogen, and separation into two liquid layers does not take place. The freezing-point curve falls rapidly at first, then slowly, and then, from 90 atomic % Na, very rapidly. The eutectic point lies not more than 0·1° below the freezing point of sodium. Solid solutions of sodium in silver are formed up to 13 atomic % Na. C. H. D.

Photo-Halides. I. WILLEM REINDERS (*Chem. Weekblad*, 1910, **7**, 961—973).—Crystalline photo-chlorides of silver have been prepared by crystallising silver chloride from dilute aqueous solutions of ammonia in presence of sunlight. The crystals were indigo-blue in colour, the depth of tint depending on the intensity of the light and the duration of the crystallisation. The darkest crystals contained about 1% of free silver. Exposure under blue glass during crystal-

lisation did not affect the colour of the resulting crystals, but with green or yellow glass the tint was much lighter, and with red glass colourless crystals were formed. During exposure to light for several days, the colour of the crystals changed to reddish-brown, and they became opaque. Longer exposure to light produced a grey colour with metallic lustre. These colour changes are caused by superficial reduction to metallic silver. The free silver present in the photo-chloride is in the colloidal state.

Crystallisation from a solution of colloidal silver was effected by addition of a small proportion of formaldehyde to a saturated solution of silver chloride in ammonia (4*N*), slow reduction to a colloidal solution of silver taking place. In transmitted light, the resulting crystals were light yellow to reddish-brown in colour, whilst in reflected light they were yellow, chocolate-brown, or green. They did not contain more than 1—2% of free silver. In diffused sunlight, they changed slowly in colour from yellow to indigo-blue, with production of intermediate shades of red, reddish-violet, and violet-blue.

A. J. W.

The So-called Emulsion of Silver Iodide. JOHN K. THUM (*Amer. J. Pharm.*, 1910, **82**, 507—508).—When silver nitrate reacts with potassium iodide dissolved in a solution of egg-albumin, the greater part of the precipitated silver iodide is maintained in colloidal solution. Irish moss mucilage gives fairly good results as a substitute for egg-albumin.

Solutions of gelatin (0·1—0·5%) in water also give good suspensions. In this medium the precipitates at first fall to the bottom of the flask, but permanent, almost perfect suspension can then be obtained by agitation, and the suspension improves on keeping.

T. A. H.

The Tellurides of Silver. GIOVANNI PELLINI and E. QUERCIGH (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 415—421).—The mixtures of tellurium and silver are melted in a current of nitrogen. The freezing-point diagram indicates the formation of two compounds, AgTe and Ag_2Te, the first being marked by a break in the curve at 444°, and the second by a maximum at 959°. There are two eutectic points, at 351° and 33·3 atomic % Ag, and at 872° and 86 atomic % Ag respectively. The compound AgTe undergoes a transformation at 412°, but a polymorphic change of Ag_2Te, which is identical with the mineral hessite, is not observed.

The alloys are crystalline and metallic in appearance, changing from grey to white as the silver increases. The brittleness diminishes from tellurium to silver. C. H. D.

The Absorption of Bromine by Lime. W. A. R. WILKS (*Proc. Camb. Phil. Soc.*, 1910, **15**, 526—528).—Solutions of bromine in carbon tetrachloride react with slaked lime with the formation of a brown product. Using weak solutions of bromine, the concentration of the bromine in the lime increases with the concentration of the solution, the ratio $C_1/C_2^{1/3}$ being sensibly constant, pointing to the

formation of an adsorption product. With more concentrated solutions of bromine, the quantity taken up is independent of the concentration, and the ratio $Ca(OH)_2 : Br = 4 \cdot 42 : 1$, indicating the formation of a compound. With dry slaked lime, the ratio soon becomes constant at $14 \cdot 9 : 1$, the equilibrium concentration of bromine being thus much lower, a result similar to that observed with bleaching powder. The colour of the product increases until the constant concentration is reached. C. H. D.

Anhydrous Sulphates. G. CALCAGNI and G. MANCINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 422—427).—The double sulphates of calcium and the alkali metals have been studied by D'Ans (Abstr., 1909, ii, 401). The freezing-point curve of mixtures of calcium sulphate and sodium sulphate has now been determined. Pure calcium sulphate decomposes so readily at 1000° that its freezing point cannot be determined, but extrapolation of the curve gives 1375°. Sodium sulphate melts at 887° and undergoes a polymorphic change at 234°; this transformation is not observed in mixtures containing more than 7% of calcium sulphate. The curve has a single maximum at 949°, corresponding with the compound $3Na_2SO_4,CaSO_4$, an analogue of vanthoffite, $3Na_2SO_4,MgSO_4$. The eutectic point is at 917° and 51% Na_2SO_4, corresponding with the composition of the mineral glauberite. It is possible that other double salts may exist at lower temperatures, especially glauberite and the pentacalcium sulphate.

Between 73% and 82·6% of sodium sulphate, two liquid layers are formed. C. H. D.

[Calcium Silicides.] ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1910, **68**, 297—300).—A reply to Hönigschmid (this vol., ii, 503) maintaining the accuracy of the author's formulæ for the calcium silicides (this vol., ii, 35). C. H. D.

The Temporary Hardness of Water. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1910, **23**, 2025—2029. Compare Abstr., 1908, ii, 435). —The solubility of calcium carbonate in water free from carbon dioxide is lessened by the presence of magnesium carbonate. Experiments are described to determine the influence of magnesium salts and of organic substances on the temporary hardness, but without definite result. C. H. D.

Preparation of Crystalline Strontium. ANTOINE GUNTZ and GALLIOT (*Compt. rend.*, 1910, **151**, 813).—A mixture of anhydrous strontium oxide with the calculated amount of aluminium is heated for four hours at 1000° in a steel tube (10 cm. long, 3 cm. diam.), which is placed in an evacuated porcelain tube. On cooling, the inner tube is found to be coated with silver-white crystals of strontium containing 99·4% of the metal. The product has D 2·63, and the yield is 75% of the theoretical. W. O. W.

Solubility of Strontium Nitrate and Strontium Hydroxide in the Presence of Each Other. CHARLES L. PARSONS and C. L. PERKINS (*J. Amer. Chem. Soc.*, 1910, **32**, 1387—1389).—The solubility

data obtained at 25° can be represented by means of two curves intersecting at a point which gives the composition of the solution saturated with respect to both substances. This solution contains 1·76 parts of strontium oxide and 81·06 parts of strontium nitrate per 100 parts of water. The curves are quite similar to those obtained in the case of barium nitrate and barium hydroxide (compare following abstract), and show that no basic nitrates of strontium are capable of existence at 25°.

H. M. D.

Solubility of Barium Nitrate and Barium Hydroxide in the Presence of Each Other. CHARLES L. PARSONS and H. P. CORSON (*J. Amer. Chem. Soc.*, 1910, **32**, 1383—1387).—These measurements were made to ascertain whether a basic barium salt analogous to the calcium salt, $CaO,Ca(NO_3)_2,3\frac{1}{2}H_2O$, is capable of being obtained.

The graphical representation of the solubility data for 25° gives two curves meeting at a point corresponding with a solution which contains 5·02 parts of barium oxide and 11·48 parts of barium nitrate in 100 parts of water. This solution is saturated with respect to both $Ba(OH)_2,8H_2O$ and $Ba(NO_3)_2$. The saturated solutions of the two substances separately contain respectively 4·29 parts of barium oxide and 10·30 parts of barium nitrate per 100 parts of water. The solubility of each substance is increased in presence of the other. The data show that basic nitrates of barium are not formed at 25°.

H. M. D.

The Action of Solutions of Borax on Zinc Salts. FRIEDRICH BORCHERS (*Zeitsch. anorg. Chem.*, 1910, **68**, 269—291).—The composition of the precipitate obtained from borax and zinc salts is very variable. The possible equilibria have now been studied in detail. The reaction may be expressed thus:

$$[B_4O_7''][H_2O]^3[Zn^{\bullet\bullet}] = k[H_3BO_3]^2[Zn(BO_2)_2].$$

The borax is employed in most of the experiments as a saturated solution, but also occasionally in the solid form or as a supersaturated solution. For the analysis, a part of the filtrate is precipitated with sodium carbonate to remove zinc, neutralised with standard hydrochloric acid with methyl-orange as indicator, and after boiling to remove carbon dioxide, glycerol is added, and the solution is titrated with potassium hydroxide, using phenolphthalein as indicator.

Boric acid does not react with zinc oxide or hydroxide to form solid zinc borate, although some zinc goes into solution, but boric acid and zinc carbonate react readily.

The largest yield of zinc borate is obtained by adding a concentrated solution of a zinc salt to a slight excess of saturated borax solution. The maximum proportion of borax thus precipitated as zinc borate is 38·6%, using solid zinc sulphate. Higher results are obtainable from supersaturated borax solution or solid borax. An excess of zinc salt diminishes the yield, complex zinc salts being formed. Indifferent salts have a similar effect, a large excess of magnesium chloride, for instance, preventing precipitation completely.

If the hydrolysis of the borax is checked by the addition of boric acid, the whole of the borax, and even a part of the added boric acid

may be precipitated by means of a zinc salt. Borax does not produce any precipitate with sodium zincoxide, but by addition of only small quantities of sodium hydroxide the precipitation is rendered more complete. If the zinc borate is removed by filtration, and an excess of sodium hydroxide, followed by zinc sulphate, is added to the filtrate, a further precipitate is obtained, and this process may be repeated until 94% of the borax has been converted into zinc salt. Sodium carbonate has less effect than sodium hydroxide, and the addition of sodium chloride or sulphate then modifies the reaction.

Manganous salts behave similarly to zinc salts. C. H. D

Hydrates of Cadmium Nitrate. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 562—567).—Cadmium nitrate, which crystallises from aqueous solution with $4H_2O$, can be obtained, like the corresponding silver salt, in the anhydrous state by the evaporation of the hydrate. Contrary to Funk's statement (Abstr., 1899, ii, 209), no salt with $2H_2O$ or $6H_2O$ could be obtained. At low temperatures, however, a salt with $8H_2O$ was produced. The *anhydrous* salt melts at about 350°, and dissolves in water with development of much heat. The solubility curve of the anhydrous salt, $Cd(NO_3)_2$, in the hydrate, $Cd(NO_3)_2,4H_2O$ (investigated in the solid condition in Flawitsky's apparatus: Abstr., 1909, ii, 886), has a break beyond the m. p. of the hydrate, 59·5°, descending to 44·5°, which is the eutectic point of the mixture, and corresponds with the composition $Cd(NO_3)_2,2{\cdot}65H_2O$; the curve then rises continuously to the m. p. of the anhydrous salt, about 350°. Z. K.

The Binary and Ternary Alloys of Cadmium, Bismuth, and Lead. WILLIAM E. BARLOW (*J. Amer. Chem. Soc.*, 1910, **32**, 1390—1412).—From observations of the rate of cooling of the molten alloys, the author has determined the freezing-point curves for the pairs of metals: lead–cadmium and lead–bismuth. By combination of these results with the data obtained in experiments on alloys containing the three metals, the solidification diagram for the ternary system has been deduced.

Lead and cadmium give rise to two curves intersecting in a eutectic point, which corresponds with 82·6% of lead and a temperature of 247·3°. On the cadmium side, the form of the curve points to a slight solubility of lead in solid cadmium, and on the lead side, cadmium appears to dissolve in the solid lead to the extent of about 3%.

Lead and bismuth yield a similar diagram, the eutectic temperature being 124·3—124·8°, and the composition corresponding with 56·5% of bismuth. On the bismuth side, the data indicate that bismuth dissolves in solid lead to the extent of about 11%.

From the very numerous observations which have been made with alloys containing the three metals, a triangular diagram has been constructed. The ternary freezing point is sharply defined at 91·4—91·5°, and the composition of the ternary eutectic is given as 40·2% lead, 51·65% bismuth, and 8·15% cadmium. H. M. D.

Equilibria in the Precipitation of Lead Hydroxide. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, **68**, 421—424).—When lead oxide is shaken with an alkali halide and water, the whole mass becomes pasty, and it is therefore necessary to approach the equilibrium from the other side. The formation of basic salts may be left out of consideration. The constant $[PbCl_2][KOH]^2/[KCl]^2$ is found to be 0·00073, and for the corresponding reactions with ammonia and methylamine, 0·00082 and 0·00066 respectively. The solubility of lead hydroxide is calculated to be $0·93 \times 10^{-4}$. C. H. D.

Basic Lead Carbonates. LEOPOLD FALK (*Chem. Zeit.*, 1910, **34**, 937—938).—When lead carbonate is shaken with a solution of basic lead acetate, three parts of carbonate withdraw two parts of oxide from solution, as shown by titration, but the washed precipitate always contains too much carbonate for the formula. If boiled with the basic lead acetate solution, the ordinary basic carbonate, $2PbCO_3,Pb(OH)_2$, is obtained.

Crystalline and amorphous lead carbonates differ in their chemical behaviour. Thus, whilst the crystalline compound reacts readily with lead oxide in presence of lead acetate, the amorphous modification only reacts very slowly. The formulæ $CO{<}^{O}_{O}{>}Pb$ and

$$Pb{<}^{O}_{O}{>}C{<}^{O}_{O}{>}C{<}^{O}_{C}{>}Pb$$

are proposed for the two modifications, and a similar polymerisation is assumed in the case of white lead. Structural formulæ for the basic carbonates are proposed.

Hydrogen sulphide only reacts very slowly with crystalline white lead, but rapidly with the amorphous variety. C. H. D.

Solubility of Lead Sulphate and Lead Chromate, and of Mixtures and Oil Colours Containing the two Salts in Dilute Hydrochloric Acid. The Equilibrium between Chromate and Dichromate in Solution. KARL BECK and PH. STEGMÜLLER (*Arb. K. Gesundh.-Amt*, 1910, **34**, 446—483).—Measurements have been made of the solubility of lead sulphate and lead chromate in 0·1*N*- to 0·6*N*-hydrochloric acid at 18°, 25°, and 37°. The data for lead sulphate show that, at constant temperature, the solubility is approximately proportional to the concentration of the hydrogen ions. In the case of lead chromate, the solubility in the more dilute solutions is nearly proportional to the hydrogen ion concentration, but in the more concentrated solutions it is more nearly proportional to the square of the concentration of these ions. The increase in solubility with rise of temperature is linear for both salts, the increase per 1° being 2·1% for the sulphate, and 3·5—4% for the chromate.

The equilibria in the solutions have been examined theoretically, and it is shown that the observed differences in the dependence of the solubility of the two salts on the concentration of the acid is due to the formation of dichromate ions in accordance with the equation:

$$2HCrO_4' = Cr_2O_7'' + H_2O.$$

In acid solutions less concentrated than 0·3*N*, the effect of this change

is not very marked, but in the stronger solutions it results in a considerable increase in the amount of lead chromate dissolved per mol. of acid present. In connexion with the analysis of the equilibrium in solution, measurements were made of the solubility of lead sulphate in 0·1 to 0·4*N*-solutions of sodium chloride and nitric acid, and of lead chromate in 0·1 to 0·6*N*-nitric acid. From these data the following equilibrium constants are calculated: $[H^{\cdot}].[CrO_4'']/[HCrO_4'] = 3{\cdot}7 \times 10^{-7}$, $[H^{\cdot}]^2.[CrO_4'']^2/[Cr_2O_7''] = 3{\cdot}4 \times 10^{-13}$, $[H^{\cdot}][Cr_2O_7'']/[HCr_2O_7'] = 1{\cdot}0 \times 10^{-3}$, $[HCrO_4']^2/[Cr_2O_7''] = 2{\cdot}5$.

Data are also recorded showing the quantities of lead dissolved by 0·1 to 0·4*N*-hydrochloric acid solutions in presence of both sulphate and chromate, and these are supplemented by observations showing the rate at which oil colours containing these two substances are attacked by dilute hydrochloric acid solutions. H. M. D.

The Ternary System Copper–Antimony–Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 343—449. Compare this vol., ii, 956).—In this paper are given the results obtained in the examination of the ternary system Cu_3Sb–Cu–Bi, the second of the two systems into which the system Cu–Sb–Bi resolves itself. The diagram constructed from them differs from that which was deduced on general grounds, because both copper and bismuth and Cu_3Sb and bismuth form eutectics which practically coincide with bismuth. Photomicrographs of some typical alloys are given. In conclusion, the space of miscibility in the liquid state is discussed, the limits of the space in the two systems being obtained by analysis of the two layers in equilibrium at about 670°, which is very near the initial temperature of solidification of alloys in that region. Uniting the two systems Cu_3Sb–Cu–Bi and Cu_3Sb–Sb–Bi in one diagram, it then becomes possible to exhibit on it the closed curve representing the boundary of the space of miscibility. All alloys within the curve separate into two layers, whilst those outside it are miscible in all proportions. R. V. S.

Action of Chlorine in Carbon Tetrachloride Solution and of Carbon Tetrachloride on Metallic Oxides. ARTHUR MICHAEL and ARTHUR MURPHY, jun. (*Amer. Chem. J.*, 1910, **44**, 365—384).—This investigation was undertaken originally with the object of ascertaining the relation between the position of metals in the periodic system and the behaviour of their unsaturated oxides towards chlorine.

The following experiments were made with a 10% solution of dry chlorine in carbon tetrachloride. With ferrous oxide, a violent action occurs, even when the chlorine solution is cooled to −18°, with formation of ferric oxide and chloride: $6FeO + 3Cl_2 = 2Fe_2O_3 + 2FeCl_3$. Manganous oxide reacts less violently; nickelous oxide reacts readily at the ordinary temperature, but the reaction is not complete for a considerable time; in the case of cobaltous oxide, the mixture must be heated at 100° in a sealed tube in order to complete the reaction. These reactions may be represented by the general equation: $3MO + Cl_2 = M_2O_3 + MCl_2$. Stannous oxide reacts violently with the solution,

with formation of stannic chloride and a light brown oxide, probably identical with the oxide, $SnO,20SnO_2$, obtained by Schiff (*Annalen*, 1861, **120**, 52) by treating stannic acid with a solution of stannous chloride. Cuprous oxide requires to be heated at 250° with the solution in order to effect a reaction; *cupric oxychloride*, Cu_2OCl_2, is thus obtained as a dark brown, amorphous powder. Antimony trioxide reacts with the chlorine solution at 100° in a sealed tube in accordance with the equation: $Sb_2O_3 + 3CCl_4 + 2Cl_2 = 2SbCl_5 + 3COCl_2$. In the case of silver oxide, the following reaction takes place at the ordinary temperature: $Ag_2O + Cl_2 + CCl_4 = 2AgCl + COCl_2 + Cl_2$. The chlorine evidently behaves as a catalyst, since when the oxide is heated with carbon tetrachloride in the absence of free chlorine, carbonyl chloride is not produced until a temperature of about 250° is reached. Lead oxide reacts with the solution at 100° in accordance with the equation: $2PbO + Cl_2 = PbO_2 + PbCl_2$. Mercuric oxide, although reacting readily with chlorine gas, even at 0°, is not affected by a solution of chlorine in carbon tetrachloride unless the mixture is heated at 100° in a sealed tube; the products thus obtained consist of mercuric chloride and some basic chlorides.

When molybdenum dioxide is heated with carbon tetrachloride in a sealed tube at 250°, it is converted into the tetrachloride. Molybdenum trioxide reacts with carbon tetrachloride at 280° with formation of the pentachloride. When the trioxide is heated with a solution of chlorine in carbon tetrachloride at 200°, the product consists of a yellowish-green oxychloride mixed with unchanged trioxide; at 225°, a mixture of yellow and green compounds is obtained, probably consisting of the dioxy-dichloride and the oxytetrachloride; at 240°, the pentachloride is produced. The pentachloride is also obtained when the oxide, Mo_3O_8, is heated with carbon tetrachloride at 240°. When tungsten trioxide is heated with the chlorine solution, the oxychloride, $WOCl_4$ is formed at 240°, and the hexachloride at 280°; in the absence of free chlorine, reaction does not occur at 240°, but at 280° the hexachloride is produced. Uranium dioxide, if heated with carbon tetrachloride at 250°, yields the tetrachloride, whilst the oxides UO_3 and U_3O_8, when heated at the same temperature, give the pentachloride. E. G.

Diffusion Phenomena of the Alums. Charles L. Parsons and W. W. Evans (*J. Amer. Chem. Soc.*, 1910, **32**, 1378—1383).—Solutions of alum, when allowed to undergo diffusion into distilled water through a parchment or agar-agar diaphragm, are more or less completely separated into the component simple sulphates. Similar results were obtained at 25° and at 0°. The separation is more complete in the case of the chrome alums than in that of the aluminium alums. The authors draw the conclusion that the dissolved alums are more or less completely resolved into the simple sulphates. H. M. D.

Composition of Some Greek Vases. William Foster (*J. Amer. Chem. Soc.*, 1910, **32**, 1259—1264).—A study has been made of the nature and composition of the black glaze of vases of the black-figured and red-figured Attic styles and the red glaze of the Mycenæan style.

The black colour of the glaze of fragments of some Greek vases was found not to be due to manganese, as has been suggested, but to the presence of ferrous iron, probably existing as silicate.

The red colour of the glaze of a fragment of a Mycenæan vase was found to be due to the presence of ferric iron.

A fragment of a vase of the Mycenæan style has been analysed, and the results are compared with those recorded for Attic and Campanian pottery. The Mycenæan pottery contains considerably less silica and much more lime than the other varieties, and yields a large quantity of carbon dioxide. The percentage of aluminium is about the same in each case, but the Campanian ware contains about twice as much ferric iron as the Mycenæan and Attic. The amount of magnesium is about the same in the Mycenæan and Attic varieties, but is much less in the Campanian. E. G.

The Structure of Cast Iron in the Graphitic Condition. OTTO KROHNKE (*Metallurgie*, 1910, **7**, 674—679).—When cast iron is transformed into the "graphitic" condition by corrosion, the ferrite is removed from the pearlite, whilst cementite and iron phosphide remain unaltered. The graphite retains its position in the mass, but is partly converted into a white or grey substance, graphitite, the composition of which is unknown. White cast iron does not undergo such a change, the constituents being resistant to corrosion. Wrought iron, although containing pearlite in small quantities, does not corrode in this way, the presence of graphite being necessary to produce the requisite electrolytic couples. C. H. D.

Case-Hardening. SYDNEY A. GRAYSON (*J. Iron Steel Inst.*, 1910, **81**, 287—302).—The case-hardening of steel by means of carbonaceous mixtures takes place best at 950—1000°. At 900—950°, diffusion being very slow, a highly supersaturated external layer is produced. Sulphur diffuses in a similar manner to carbon at the same temperature. C. H. D.

The Crystallography of the Iron-Carbon System. ADOLPHE KROLL (*J. Iron Steel Inst.*, 1910, **81**, 304—385).—When steel is heated and cooled in an inert gas, relief-patterns are obtained indicating the volume changes which have taken place at the critical points. The microscopical examination of etched sections shows that ordinary cementite is hexagonal, but that the carbide entering into solution in γ-iron is regular. A modified equilibrium diagram is proposed, in which a gap exists between two series of solid solutions, one of carbide in γ-iron and one of γ-iron in cementite, the latter solution being identical with troostite. This system is formed in tempering. A theory of the constitution of iron-carbon alloys, based on the crystallographic development, is proposed for the metastable systems, the only stable chemical equilibrium being that of ferrite and graphite. C. H. D.

The Influence of Sulphur on the System Iron-Carbon. THEODOR LIESCHING (*Metallurgie*, 1910, **7**, 565—571).—The distribu-

tion of iron sulphide in alloys of iron and carbon has been studied microscopically. The ferrous sulphide appears in low-carbon alloys in the form of thin films surrounding the crystals of ferrite. When the sulphur exceeds 2% in an alloy high in carbon, two liquid layers are formed, of which the lighter sulphide layer does not contain carbon. C. H. D.

The Influence of Silicon on the Maximum Solubility of Iron Carbide in γ-Iron. CH. SCHOLS (*Metallurgie*, 1910, **7**, 644—646).—The solubility of iron carbide in γ-iron is known to be diminished by the addition of silicon. Thermal and microscopical investigations of alloys prepared from iron and ferro-silicon show that the maximum solubility, which is at 2·2% C in the absence of silicon, is lowered to 1·9% by 1·34% Si, to 1·5% by 1·8% Si, and to 1·2% by 5·6% Si. The eutectic point remains constant at 1120°. The pearlite transformation point is slowly raised by the addition of silicon, but becomes imperceptible above 1·2% C if the alloy contains 5·6% Si, or above 1·5% C in the presence of 4·5% Si. C. H. D.

Iron, Manganese, and Carbon. JOHN O. ARNOLD and ARTHUR A. READ (*J. Iron Steel Inst.*, 1910, **81**, 169—181).—The carbides isolated from alloys of iron, manganese, and carbon by electrolysis show an increase in the ratio of manganese to iron as the proportion of manganese in the alloy is increased, becoming constant in steels containing from 4·98 to 13·38% Mn, afterwards increasing still further. The results do not decide whether double carbides or a mixture of the two carbides are present. Tested by the colour test, carbides of this kind indicate a lower percentage of carbon than pure iron carbide. Up to 10% Mn, the colour is only that due to the iron carbide present, showing that manganese carbide does not give a coloration with nitric acid, D 1·20. Alloys containing 11 or 14% Mn give a higher coloration with nitric acid. C. H. D.

Some Physical Properties of 2% Chromium Steels. ANDREW MCWILLIAM and ERNEST J. BARNES (*J. Iron Steel Inst.*, 1910, **81**, 246—267).—The thermal analysis of steels containing 2% of chromium and varying quantities of carbon shows that the critical point *Ac*2 is depressed below *Ac*1 when the carbon is between 0·2 and 0·5%. The three critical points become identical in steels containing 0·65 or 0·85% C. The saturation point lies between the last two values. The microscopic structure does not indicate the form in which the chromium is present in the steel. C. H. D.

The Ac2 Point in Chromium Steel. HAROLD MOORE (*J. Iron Steel Inst.*, 1910, **81**, 268—275).—The determination of the critical points of steels containing more than 3% of chromium shows that the position of *Ac*1 is progressively raised by the addition of chromium, and that a new critical point appears below *Ac*1. The fact that the new point coincides with the temperature at which the magnetic properties of the steel disappear on heating, proves it to be identical with *Ac*2. An electromagnetic method is employed to determine this point (compare preceding abstract). C. H. D.

Reduction of Ferric Oxide by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1910, **151**, 644—645. Compare this vol., ii, 215).—The authors have studied the speed of reaction between ferric oxide and carbon at low pressures (0·001—8 mm.) to avoid as far as possible the catalytic action of gases. The mode of procedure was similar to that employed when examining the cementation of iron under similar conditions. The conclusion drawn is that carbon is incapable of reducing ferric oxide below 950°, a temperature considerably higher than has hitherto been supposed necessary. W. O. W.

The System Nickel–Sulphur. KARL BORNEMANN (*Metallurgie*, 1910, 7, 667—674. Compare Abstr., 1908, ii, 292).—The experiments with mixtures high in nickel have been repeated, using magnesia vessels and quartz protecting tubes for the thermo-couples. Care being taken to avoid undercooling, the break in the freezing-point curve formerly observed at 4 atomic % S disappears, and only a single series of solid solutions rich in nickel is observed, extending from 0 to 0·5 atomic % S. The complicated transformations in the solid state are confirmed. C. H. D.

Preparation of Anhydrous Chromic Chloride by Bourion's Method. JOSÉ RODRIGUEZ MOURELO (*Anal. Fis. Quim.*, 1910, 8, 196—199).—Although chlorine in presence of carbon attacks chromium sesquioxide prepared by gently igniting chromium hydroxide, it is without action on the crystalline sesquioxide or the sesquioxide obtained by ignition at a high temperature. But by Bourion's method (Abstr., 1909, ii, 220) these indifferent substances are rapidly converted into beautifully crystalline scales of chromic chloride; it is only necessary to pass the vapour of sulphur chloride (b. p. 137—139°) over the oxide heated gradually to a red heat, and, after the action is complete, to cool in a current of dry hydrogen chloride. W. A. D.

Uranium Salts. I. and II. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 570—581).—Uranium nitrate gives three hydrates, $UO_2(NO_3)_2,6H_2O$, $UO_2(NO_3)_2,3H_2O$, and the *dihydrate*, $UO_2(NO_3)_2,2H_2O$, but the nitrate, $UO_2(NO_3)_2,1\frac{1}{2}H_2O$, does not exist. The hydrate, $UO_2(NO_3)_2,6H_2O$, melts at 60·2°, and when further heated just above this temperature, is transformed into the trihydrate, but if heated at a higher temperature a *basic* salt is formed, which, however, dissolves in water to a yellow solution.

The trihydrate, m. p. 121·5°, forms crystals belonging to the monoclinic system, and can also be obtained by crystallising a strongly acid solution of the sesquihydrate in nitric acid (D 1·4). The *dihydrate*, m. p. 179·3°, forms small, thick, square plates, probably of the rhombic system, very bright and with a green fluorescence. It is formed when the sesquihydrate is kept for some time in a desiccator at the ordinary temperature, or when the latter hydrate is treated thus at 100°, and the product, which now contains slightly less than $2H_2O$, is dissolved in nitric acid, D 1·502, and then allowed to crystallise. When the substance containing less that $2H_2O$ is treated

with water, the sesquihydrate separates. Tables and a curve are given for the solubility of the sesquihydrate in water, and the theoretical significance of these are discussed. Contrary to Oechsner de Coninck's statement (Abstr., 1901, ii, 104), the constitution of the solution at 13·5° is about $UO_2(NO_3)_2+19H_2O$. The constitution of the cryohydrate is $UO_2(NO_3)_2,28·93H_2O$ at $-18·1°$.

Uranium nitrate is one of those salts for which the number representing the degree of dissociation increases with increasing concentration of the solution. Z. K.

The Solution and Precipitation of Titanic Acid. Karl Bornemann and H. Schirmeister (*Metallurgie*, 1910, 7, 646—649).—Contrary to the usual statement in text-books, titanic acid which has been heated to 1000° is practically insoluble in sulphuric or hydrofluoric acid. It the temperature of ignition does not exceed 700°, solution in concentrated sulphuric acid is complete in fifteen minutes. Hydrofluoric acid has a rather greater solvent power.

Fusion with potassium hydrogen sulphate readily brings about complete solution. It is not necessary to dissolve the product in cold water, for if dilute sulphuric acid (1 : 2) is used, solution takes place completely even if the liquid is boiled. After fusion with alkali carbonate and solution in hydrochloric acid, the residue is difficult to wash, and readily passes through the filter. This is avoided by the use of sulphuric acid (1 : 2) instead of hydrochloric acid.

Orthotitanic acid may be precipitated from hot strongly acid solutions by the addition of ammonia without destroying its solubility in dilute acids. When metatitanic acid is dissolved in concentrated sulphuric acid, boiling for more than a few minutes must be avoided, or an insoluble precipitate is formed. No difference in this respect is observed between ortho- and meta-titanic acids. C. H. D.

Zirconia and Erbia from Titanium Minerals. Karl A. Hofmann (*Ber.*, 1910, 43, 2631—2636).—Hauser and Wirth have found that the zirconia contained in a number of zirconium minerals is not accompanied by a strange earth (this vol., ii, 713); the author finds that the principal mineral investigated by him, which differs from typical euxenite in that it has a very high titanium content, contains zirconia, which gives some strange lines in the arc-spectrum, and also has a higher equivalent weight than zirconia prepared from zirconium silicate

The mineral used was euxenite from Brevig, and had the composition :

Cb_2O_5.	TiO_2.	Rare earths.	SiO_2.	PbO.	ZrO_2	Fe_2O_3.	UO_8.	CaO	Loss on heating
4·65	45·74	36·17	0·53	0·33	2·83	2·06	2·73	1·60	2 80%

The rare earths comprised didymium, erbium, and holmium. The zirconia was identified by the preparation of the double fluoride with potassium, and from the mother liquors obtained in the recrystallisation of this salt zirconia was prepared, the arc-spectrum of which showed unknown lines (4519·6, 4322·65, 3682·43, 3662·29, 3253·83,

3194·30, and 3031·32), together with the known lines due to zirconium and titanium. These lines still persisted after the titanium had been removed.

The remainder of the paper deals with neo-erbium compounds. The erbium compounds contained in the rare earths mentioned above are purified from holmium and dysprosium by fractional crystallisation of the ammonium double oxalate (compare Abstr., 1908, ii, 189). Fractional crystallisation of the acetylacetone compound from alcohol may also be used. Thulium and ytterbium may be readily separated from almost pure erbium sulphate by heating to 845° for ten hours; on treating the residue with water, the less basic portions remain undissolved. The solution is evaporated to dryness, the residue heated to 950° for thirty minutes, and then treated with water, when erbium oxide remains undissolved.

By using the above methods, an erbium material was obtained, which gave a constant spectrum and a constant equivalent weight. After freeing it from impurities derived from the vessel used, a bright rose-red *oxalate* was obtained, $Er_2(C_2O_4)_3,10H_2O$. Former analyses have given $9H_2O$. On drying in a vacuum over phosphoric oxide, the *trihydrate* is formed. The oxide results on heating the oxalate to 575°; it is obtained pure at 845°, and then forms a rose-coloured powder, which does not glow in cathode rays, but gives a green, discontinuous light in the bunsen flame. The reflexion spectrum is not altered by dilution with other oxides when no compound is formed.

Atomic-weight determinations were made by transforming the sulphate into the oxide by heating at 1055°, and gave the mean value 167·68 (three determinations, O = 16, S = 32·07). At 845° a *basic sulphate*, Er_2O_3,SO_3, is obtained. T. S. P.

Colloidal Zirconium Silicide. EDGAR WEDEKIND (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 249—251).—Zirconium silicide, obtained by the action of excess of silicon on potassium zirconium fluoride in the electric furnace, has been converted into a colloidal form by Kužel's method. The finely divided substance was treated successively with dilute acid and alkaline solutions at a temperature of 50—60°, the treatment in each case being continued for about twenty-four hours. After a considerable number of such operations, a dark brown colloidal solution of the silicide is obtained. Under the microscope, the solution, which has been kept for some time, appears to be homogeneous, but the want of homogeneity is clearly seen in the ultra-microscope. The colloidal particles move towards the positive pole, and are therefore negatively charged. On the other hand, colloidal zirconium is positively charged, and coagulation takes place when solutions of the metal and of the silicide are mixed. Colloidal zirconium silicide is coagulated by various electrolytes, but in comparison with the colloidal metal, it is not at all readily acted on by solutions of alkali hydroxides. Coagulation of the silicide is also brought about by freezing the solution, and in this respect also it differs from the colloidal solution of zirconium. H. M. D.

Basic Thorium Sulphate. OTTO HAUSER (*Ber.*, 1910, **43**, 2776—2778).—The author claims priority to Barre (this vol., ii, 718) in showing that Demarcay's salt (*Compt. rend.*, 1860, **96**, 728), $3Th(SO_4)_2,ThO(SO_4),4H_2O$, is really a mixture of $Th(SO_4)_2,2H_2O$ and $ThO(SO_4),2H_2O$ (compare Abstr., 1909, ii, 54). He also confirms Barre's result that at 100° the stable basic sulphate has the composition $ThO(SO_4),2H_2O$. At 125—180° the stable basic sulphate is $ThO(SO_4),H_2O$. The author's and Barre's results show that in moderately dilute solutions of thorium sulphate the basic sulphate, $ThO(SO_4)$, is produced, which, according to the temperature, crystallises with one or two molecules of water. In very dilute solutions the sulphate may be completely hydrolysed to the hydroxide. T. S. P.

Preparation of Vanadium. WILHELM PRANDTL and BENNO BLEYER (*Ber.*, 1910, **43**, 2602—2603. Compare Abstr., 1909, ii, 1022). —Vanadium may readily be obtained by the thermite reaction, using the following mixture: 100 parts of fused and powdered vanadium pentoxide, 49·5 parts of aluminium powder, 20 parts of calcium fluoride. The action is carried out in a magnesia crucible, or, better still, in a box made of fluorspar. In the latter case it is not necessary to add the calcium fluoride to the reaction mixture.

The vanadium regulus obtained is 70—80% of the theoretical quantity, and is 95% pure. The impurity is chiefly oxygen; possibly a lower oxide of vanadium remains dissolved in the excess of vanadium and escapes the reducing action of the aluminium. T. S. P.

Red Platinum as Analogue of Purple of Cassius. LOTHAR WOHLER and A. SPENGEL (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 243—249).—Experiments have been made to determine the cause of the red colour which appears when solutions of platinum salts are acted on by stannous chloride. These show that the red substance consists of colloidal metallic platinum in a very fine state of subdivision, and that the formation of this in place of the more usual brown colloidal metal is due to the action of stannic chloride and its products of hydrolysis as protective colloids. The red colloid is also formed when the reduction of platinum salts is effected by means of a solution of phosphorus in ether, if gelatin is added as a protective colloid. The identity of the two red substances has been established by spectroscopic observations.

If the colloidal solution obtained by reduction with stannous chloride is shaken up with ethyl ether or ethyl acetate, the organic solvents take up the red colour, and this is found to be connected with the solubility of stannic chloride in these media, in which it plays the part of protective colloid.

When the aqueous solution is diluted with a large volume of water, or when the ethyl acetate solution is poured into water, a chocolate-brown precipitate is obtained. According to Schneider (*Ann. Phys. Chem.*, 1869, [ii], **136**, 105), this substance has the composition $Pt_2Sn_6O_{10}$. It is now found, however, that no definite compound is formed, but that the composition of the precipitate varies very considerably with the conditions under which it is produced. Analogous

to purple of Cassius, it appears to be a mixture of colloidal platinum and colloidal stannic acid, and this view is supported by the similarity in the properties of the two substances.

The blood-red colour which appears on reduction of silver nitrate by stannous nitrate in dilute nitric acid solution is similarly due to colloidal silver, and not to the formation of what have been described as silver stannates. On account of the instability of the red colloidal silver, the red solution quickly turns brown, and deposits a reddish-brown precipitate. The red modification of silver cannot be obtained by reduction by means of an ethereal solution of phosphorus.

H. M. D.

Mineralogical Chemistry.

Probable Identity of Podolite with Dahllite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], **30**, 309—310).—A comparison of the characters and analyses of dahllite (Brögger and Bäckström, Abstr., 1890, 714) and of podolite (W. Tschirwinsky, Abstr., 1907, ii, 481) [=carbapatite of P. N. Tschirwinsky, 1906] suggests the identity of these minerals. The composition of dahllite was expressed as $2Ca_3P_2O_8,CaCO_3,\frac{1}{2}H_2O$ ($=H_{10}Ca_{70}P_{40}C_{10}O_{195}$), and of podolite as $3Ca_3P_2O_8,CaCO_3$ ($=Ca_{70}P_{42}C_7O_{189}$). L. J. S.

Action of Carbon Tetrachloride Vapours on Minerals and Application to Quantitative Analysis. PAUL JANNASCH (*Ber.*, 1910, **43**, 3135—3136).—A claim for priority over Camboulives (this vol., ii, 202; compare Abstr., 1909, ii, 728, 767). The following analyses of a fluorapatite from Renfrew County (Ontario) are given:

P_2O_5.	CaO.	MgO.	Fe_2O_3.	K_2O.	Na_2O.	H_2O.	F.	Deduct from O for F.	Total.
39·68	54·67	1·34	0·49	0·50	0·92	0·12	3·75	−1·57	99·90
39·74	54·74	1·22	0·48	0·47	0·90	0·10	3·68	−1·54	99·78

T. S. P.

Identity of Stelznerite with Antlerite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], **30**, 311—312).—For the orthorhombic stelznerite from Chili, described by Arzruni and Thaddéeff (Abstr., 1899, ii, 563), the formula was given as $CuSO_4,2Cu(OH)_2$, whilst for the massive antlerite from Arizona, described by Hillebrand in 1889, the formula $3CuSO_4,7Cu(OH)_2$ was deduced. A microscopical examination of the latter shows that its optical characters, so far as these can be determined, do not differ from those of stelznerite, and it is pointed out that the analyses of antlerite approximate to the simpler formula. The name antlerite having priority, it is suggested that this should stand for the species [but how far this rule should apply in the case of incompletely described or incorrectly determined minerals is doubtful]. L. J. S.

New Kind of Vanadate in the Cupriferous Deposit of Bena (d)e Padru, near Ozieri (Sassari). DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 326—333).—Analysis of the new mineral by Silvio Manis gave :

V_2O_5.	P_2O_5.	PbO.	ZnO.	CuO.	Fe_2O_3.	MnO.	H_2O.	Total.
19·87	0·18	53·76	2·45	13·13	6·54	0·05	3·45	99·43

Its hardness is inferior to that of calcite, and it has $D^{10·5}$ 5·716.

R. V. S.

Further Occurrences of Tantalum and Columbium in Western Australia. EDWARD S. SIMPSON (*Austral. Assoc. Report*, 1909, 310—315).—The following analyses are given : (I) Fergusonite from Cooglegong, D 5·82—6·65 ; (II) Euxenite from Cooglegong, D 5·37 ; (III) Microlite from Wodgina, D 5·422 ; (IV) Ixiolite (?) from Wodgina, D 7·36 ; (V) Casseterite from Greenbushes.

	Ta_2O_5.	Cb_2O_5.	TiO_2.	SnO_2.	ThO_2.	Y_2O_3.	Er_2O_3.	Ce_2O_3.	La_2O_3, Di_2O_3	CaO.
I.	55·51	2·15	2 20	—	1·02	23·00	8·38	0·94	—	2·18
II.	23·10	4·35	30·43	—	1·76	15·76	9·27	1·82	1·73	1·02
III.	73·54	3·62	—	0·90	—	—	—	—	—	13·46
IV.	70·49	7·63	—	8·92	—	—	—	—	—	0·42
V.	1·76	—	—	97·63	—	—	—	—	—	—

	FeO.	MnO.	MgO.	UO_3.	Al_2O_3.	K_2O.	Na_2O.	Ignition.	Total.
I.	trace	0·87	—	1·18	—	—	—	3·36	100·79
II.	trace	0·34	0·35	6·69	0·76	—	—	2·82	100·20
III.	3·64	0·60	0·42	—	—	0·20	1·66	1·28	99·32
IV.	1·34	10·87	0·37	—	—	—	—	0·18	100·22
V.	0·61	—	—	—	—	—	—	—	100·00

The analytical results for fergusonite agree with the usually accepted formula, R_2O_3,Ta_2O_5 ; those for ixiolite, with the formula $3MnO,3Ta_2O_5,SnO_2$.

T. S. P.

Analysis of a Fossil Wood. F. HART (*Chem. Zeit.*, 1910, **34** 1168).—A fossil palm-tree, found in a bed of clay of Miocene age at Cuxhaven on the Oste, a small tributary of the Elbe, gave :—

		Insol. in HCl		Soluble in HCl						
Moisture.	CO_2,H_2O*.	SiO_2.	$(Al,Fe)_2O_3$.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3	Alkalis and diff.
1·45	8·21	51·72	0·26	0·25	26·80	2·68	7·04	0·21	0·23	1·15

* Organic matter soluble in soda was also present.

Two samples of the clay gave :

SiO_2.	$(Al,Fe)_2O_3$.	CaO.	MgO.	SO_3.	Loss on ignition.
50·45	30·00	1·86	2·50	0·60	14·40
60·50	26·60	2·00	2·50	0·60	7·95

The ratio of silica to sesquioxides is very nearly the same in the fossil as in the first of the clay analyses (namely, 1·76 and 1·68 respectively ; in the second clay analysis it is, however, 2·27) ; but whilst in the clay the sesquioxides are insoluble in hydrochloric acid, in the fossil they are almost wholly soluble. To explain this, it is suggested that at the time of the deposition of the clay, when this was suspended in a very finely divided state or in colloidal solution, the

cellular organic matter of the wood exerted an adsorptive action, and resolved the clay into aluminium hydroxide and hydrated silica.

L. J. S.

Barbierite, a Monoclinic Soda-felspar. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], **30**, 358—359).—Barbier and Prost (Abstr., 1908, ii, 863) have recently established the existence of a monoclinic soda-felspar ($NaAlSi_3O_8$) isomorphous with orthoclase and dimorphous with albite. For this the name *barbierite* is proposed. The felspar from Kragerö with only 1·15% K_2O is nearly pure barbierite. Other analyses of soda-rich orthoclases have been given by Barbier (this vol., ii, 419).

L. J. S.

[Minerals in Dacite from Victoria.] ERNEST WILLINGTON SKEATS (*Quart. J. Geol. Soc.*, 1910, **66**, 450—468).—In a description of the rocks of the Dandenong district, the following analyses, by Plante and Richards, are given of dacite (I) from Upway, and of the minerals isolated from this, namely, biotite (II), formula

$$2(K,H)_2O,4(Fe,Mg)O,Al_2O_3,6(Si,Ti)O_2;$$

hypersthene (III), formula $12(Fe,Mg)O,(Al,Fe)_2O_3,16SiO_2$; ilmenite (IV), formula $(Fe,Mg)O,2TiO_2$.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O. (105°).	H_2O. (>105°).	P_2O_5.	Total.	Sp. gr.
I.*	63·27	1·30	16·50	0 68	5·10	0 03	4·18	2·48	2 68	2 36	0 09	0·52	0·15	99·50	2·76
II.†	39 86	7 95	11·13	1·39	18·10	0 58	trace	9·88	6·73	0·35	0·43	3·20	trace	99·60	3 16
III.	50·42	3·51	4·06	2·10	23·54	0·24	1·30	13·04	0·69	trace	0 10	0·6	0·92	99·98	3·36
IV.	—	67·28	—	—	31·92	trace	—	0·80	—	—	—	—	—	100·00	4·86

* Also S (in pyrites), 0·16; Li_2O, trace. † Also Li_2O, trace.

L. J. S.

[Minerals Associated with Diamond in Rhodesia.] FREDERIC PHILIP MENNELL (*Quart. J. Geol. Soc.*, 1910, **66**, 353—375).—In a description of the geological structure of Southern Rhodesia, the following analyses, by W. C. Hancock, are given of minerals from the "blue ground" of the new Colossus diamond mine, thirty-five miles north-east of Bulawayo: I, deep red pyrope; II, small, orange-coloured garnets from eclogite fragments in the "blue ground"; III, a more reddish garnet, also from eclogite; IV, deep green augite (chrome-diopside), with a pronounced parting parallel to the ortho-pinacoid.

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	40·43	19·13	2·12	4·94	8·66	0·12	4·44	20·33	—	100·17	3·72
II.	40·44	23·69	0·32	6·51	11·38	0·60	9·86	7·72	—	100·52	3·75
III.	39·87	21·47	0·26	4·95	8·10	0·23	12·32	12·89	—	100·09	3·64
IV.	53·93	1·90	0·70	5·97	2·67	—	13·11	20 08	1·63	99·99	—

L. J. S.

The Nature of the Pseudonepheline from Capo di Bove, near Rome. FERRUCCIO ZAMBONINI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii*a*], **16**, 83—86).—The pseudonepheline or pseudo-sommite of Capo di Bove has been re-examined. The crystallographic

characters agree with those of nepheline, but the refractivity is rather higher and the double refraction lower. Analysis shows:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Total.
39·91	33·04	2·14	2·55	12·75	10·06	100·45

corresponding with $(Na,K)AlSiO_4$, whilst nepheline always contains a higher proportion of silica. Pseudonepheline has, therefore, a composition between that of kaliophilite, $KAlSiO_4$, and the silicate, $NaAlSiO_4$, which has only been obtained artificially. C. H. D.

Physiological Chemistry.

Relative Influence of the Heat and Chemical Impurity of Close Air. LEONAND E. HILL, R. A. ROWLANDS, and H. B. WALKER. **The Influence of Alcohol on the Power to Hold the Breath and Work.** J. F. MACKENZIE and L. E. HILL. **Compressed-air Illness. I. Solubility of Compressed Air in Water and Oil.** J. F. TWORT and L. E. HILL. **II. The Desaturation of the Arterial Blood as Measured by the Nitrogen Dissolved in the Urine.** L. E. HILL, J. F. TWORT, and H. B. WALKER. **Effect of Breathing Oxygen on the Nitrogen and Oxygen of the Urine.** L. E. HILL, J. F. TWORT, H. B. WALKER, and R. A. ROWLANDS (*Proc. physiol. Soc.*, 1910, iii—iv, iv, v—vi, vi—vii, viii; *J. Physiol*, 41).—In hot closed chambers with no ventilation the discomfort is caused by moisture rather than by chemical impurities. Half an ounce of alcohol extends the time during which a man can hold his breath while performing work. Various results showing that air is more soluble in oil than water are confirmed; fat men should be excluded from caisson work. During decompression, the nitrogen in the urine sinks; the nitrogen does not get into equilibrium with the atmospheric pressure under ten to fifteen minutes. During the breathing of oxygen the renal epithelium checks its entry into the urine; some of the dissolved nitrogen can be got out of the body by this means, but not so much as was expected. W. D. H.

A Respiration Apparatus for Isolated Organs and Small Animals. OTTO COHNHEIM. **The Gaseous Metabolism of the Musculature of the Small Intestine.** O. COHNHEIM and DIMITRI PLETNEFF. **The Gaseous Metabolism of the Stomach Musculature.** O. COHNHEIM and D. PLETNEFF. **The Gaseous Metabolism of the Musculature of Stomach and Intestine during Insufficient Oxygen Supply and under the Influence of Barium Chloride.** O. COHNHEIM and D. PLETNEFF (*Zeitsch. physiol. Chem.*, 1910, **69**, 89—95, 96—101, 102—105, 106—107).—The apparatus described was constructed on the principle of the Atwater-Benedict machine, and was used in the experiments on stomach and

intestine which follow. The intestine of cats is treated with mercuric chloride, which destroys the cells of the mucous membrane and bacteria, but leaves the muscle in active movement in Ringer's solution. This produces 80—90 mg. of carbon dioxide per 100 grams of intestine per hour, and uses up a corresponding amount of oxygen. The gaseous metabolism is furthered if oxygen is circulated direct through the capillaries. The respiratory quotient is 0·78.

In the stomach musculature in strong activity, 170—175 mg. of carbon dioxide are produced per 100 grams per hour.

In a previous research on intestinal muscle (Abstr., 1908, ii, 209) a smaller figure was given. This is due to insufficient oxygen supply, and not to the use of barium chloride in the experiments, for that salt does not affect the amount of carbon dioxide produced.

No reference is made to the work of Brodie and others on gaseous metabolism of the small intestine during rest and activity (this vol., ii, 518). The figures there given are in terms of c.c. per gram per minute. Cohnheim's figures for the intestine muscle (85 mg. of carbon dioxide per 100 grams per hour) may be reduced to the same terms and compared with Brodie's:

c.c. of carbon dioxide in intestinal muscle : 0·0071 (Cohnheim).
,, ,, ,, ,, whole small intestine at rest: 0·02 (Brodie)
,, ,, ,, ,, epithelial cells of small intestine : 0·0318 (Brodie's estimate).

Brodie's further estimate is taken as fairly accurate that the muscular coat accounts for 40%, and the mucous membrane of the small intestine for the remaining 60%. If 60% of the intestine is producing carbon dioxide at the rate estimated by Brodie, and the remaining 40% at the rate determined by Cohnheim, the whole intestinal wall will produce 0·23 c.c. of carbon dioxide per gram per minute; that is to say, a figure is obtained a little higher than that actually determined by Brodie and his colleagues. The correspondence is, however, very close, taking into account that in Cohnheim's experiments the muscle was in active movement.

The research illustrates again the low metabolism of muscle as compared with secreting epithelium. W. D. H.

Composition of the Blood-gases in Chloroform Anæsthesia. George A. Buckmaster and John A. Gardner (*J. Physiol.*, 1910, **41**, 246—262).—The total gas in the blood of cats as compared to dogs is low (this vol., ii, 969); as anæsthesia deepens this is increased, and the increase is mainly due to carbon dioxide. The amount of oxygen sinks, and the blood is dark in colour; this is probably because the chloroform unites with the hæmoglobin, and so prevents it combining with so much oxygen. This may explain the effect on the respiratory centre. Full analytical details are given, including the amount of chloroform in the blood. W. D. H.

The Permeability of Red Blood-corpuscles in Physiological Conditions, especially to Alkali and Alkali-earth Metals. Hartog J. Hamburger and F. Bubanović (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 258—270).—If a disturbance within physiological limits in

the composition of the blood is produced between the corpuscles and serum, a redistribution of the inorganic constituents takes place, both as regards anions and cations. Thus, if 0·2% sodium chloride is added to serum, sodium, magnesium and calcium enter the corpuscles, and potassium leaves them. If the serum is diluted with 10% of water, sodium enters, whereas potassium, magnesium and calcium leave the corpuscles. Calcium enters the corpuscles when the blood is shaken with 5 vols. % of carbon dioxide. The fact that the corpuscles are permeable to cations is against the current view, which is based on Grüber's work. Grüber's methods and results are criticised.

W. D. H.

Comparative Investigations on the Rotatory Properties of the Plasma and Serum of Dog's Blood under Varying Conditions. I. EMIL ABDERHALDEN and PAUL KAWOHL. II. E. ABDERHALDEN and PAUL HAHN (*Zeitsch. physiol. Chem.*, 1910, **69**, 1—22, 50—56).—I. Plasma has a stronger lævorotatory power than serum. Repeated bleedings lower the rotation in both fluids, but the change is not a great one. Feeding on 50—500 grams of meat causes no more change than occurs without feeding; there is no rise in the rotatory power. Some preliminary experiments on feeding with carbohydrates are also given, but no noteworthy effect is seen unless large amounts of monosaccharides are given; thus lævulose raises, and dextrose depresses, the lævorotation. Hunger causes considerable variations, but nothing typical. There is no difference between the optical properties of carotid and jugular blood, but the portal blood has always a higher rotation than that from other parts.

II. Injection of dextrin into the blood stream lowers the lævorotation, but the effect passes off in about twenty minutes. The lowering of rotation produced by bleeding lasts longer in fasting than in well-fed animals. W. D. H.

The Influence of Large Quantities of Water on the Optical Properties of Blood-plasma and Serum. EMIL ABDERHALDEN and ERNST RUEHL (*Zeitsch. physiol. Chem.*, 1910, **69**, 57—59).—Large quantities of water were given by the alimentary canal, and this caused a noteworthy sinking of the rotatory power of the plasma and serum; this lasts for about four hours. W. D. H.

A Method for Drying Serum. SIGMUND FRÄNKEL and ALADAR ELFER (*Biochem. Zeitsch.*, 1910, **28**, 330—331).—Attempts by various methods of evaporation do not yield good results. A perfectly dry powder was obtained by the addition of anhydrous sodium sulphate (670 grams per litre of ox-serum). W. D. H.

Autolysis of Normal Blood. J. C. SCHIPPERS (*Biochem. Zeitsch.*, 1910, **28**, 418—426).—Defibrinated blood undergoes autolysis, which is accelerated by acetic acid; proteoses, leucine, and tyrosine were found in the autolysed fluid. The active agent is destroyed by heat. The change is believed, however, to be, in part, due to a spontaneous cleavage of the protein molecule. Blood-serum shows no autolysis, but the red corpuscles do. W. D. H.

Hæmolysis. II. Hæmolysis by Sodium Carbonate. OSKAR GROS (*Arch. exp. Path. Pharm.*, 1910, **63**, 341—346. Compare this vol., ii, 51).—Hæmolysis produced by sodium carbonate runs on the same lines as that caused by ammonia. Within definite limits of concentration, the time of induction is inversely proportional to the concentration of the salt, and proportional to the amount of blood.

W. D. H.

The Hydrochloric Acid of the Gastric Juice of the Selachian Fishes. ERNST WEINLAND [with A. GROHMANN and TH. STEFFEN] (*Zeitsch. Biol.*, 1910, **55**, 58—69).—The method of Sjöqvist for estimating hydrochloric acid is not practicable in the presence of chlorides of the alkali earths. Hydrochloric acid is found even though none be present in the free state if an organic acid is present also. The gastric juice of the dog fish and other selachians contains little or no free hydrochloric acid. Statements to the contrary are due to the non-recognition of the two facts mentioned above. W. D. H.

Variations in Quantity and Composition of the Pancreatic Juice during Secretions Provoked by Secretin. S. LALOU (*Compt. rend.*, 1910, **151**, 824—827).—Repeated injection of secretin into dogs enables a regular supply of the pancreatic fluid to be obtained during several hours. The alkalinity and diastatic activity of the juice thus obtained gradually diminishes, however, the variation in lipolytic power being more marked than the diminution in tryptic or amylolytic activity. W. O. W.

Physiology of Digestion. II. Total Chlorine of the Animal Body. RUDOLF ROSEMANN (*Pflüger's Archiv*, 1910, **135**, 177—195. Compare Abstr., 1907, ii, 706).—The author's previous work on the hydrochloric acid of the gastric juice led to the present research. The methods used and results obtained by previous workers are summarised. The fœtus is richer in chlorine than the new-born animal, and the percentage amount diminishes still more after birth. The author's values for the fully-grown dog average 0·12% of chlorine. In the cat and mouse, the figure is a little higher. W. D. H.

Metabolism Experiments as Statistical Problems. H. L. RIETZ and H. H. MITCHELL (*J. Biol. Chem.*, 1910, **8**, 297—326).—Metabolism experiments should be studied mathematically, as observations on heredity are, in order to exclude the deviations which occur in physiological processes, and take place although surrounding conditions are made as constant as possible. W. D. H.

Metabolism of Development. II. Nitrogen Balance during Pregnancy and Menstruation in the Dog. JOHN R. MURLIN (*Amer. J. Physiol.*, 1910, **27**, 177—205. Compare this vol., ii, 729).—Menstruation causes a retention of nitrogen, which is to be regarded, in part, as a compensation for the blood lost. The first half of normal pregnancy is characterised by a loss of nitrogen from the mother's body. This is probably due to the action of proteolytic enzymes

produced by the embryo and not yet limited by the placenta in their action to the maternal blood. Nitrogen retention occurs in the last half of the pregnancy. W. D. H.

The Importance of the Mechanical Part of the Work of Digestion in Relation to Metabolism in the Ox. KARL DAHM (*Biochem. Zeitsch.*, 1910, **28**, 456—503).—A very important contribution to the much discussed question as to whether the work of the digestive organs is an important factor in metabolism, as Zuntz maintains, or not. A number of oxen were fed on different diets, and their metabolism and heat production determined by examining fæces, urine, and gaseous interchanges. The results confirm Zuntz's views.

W. D. H.

Digestion of Cellulose in Dogs, and the Methods for Estimating Cellulose. HANS LOHRISCH (*Zeitsch. physiol. Chem.*, 1910, **69**, 143—151).—The author's previous conclusion that dogs are able to digest cellulose, he finds on further work to be incorrect. Dogs do not digest cellulose. He still holds, however, that cellulose is digestible to some extent by man in spite of the criticisms of Scheunert. The Simon-Lohrisch method for the estimation of cellulose is regarded as the best. W. D. H.

The Work of Digestion after Carbohydrate Food, and its Dependence on the Physical Condition of the Nourishment. OTTO MÜLLER (*Biochem. Zeitsch.*, 1910, **28**, 427—455).—Investigations on the gaseous metabolism of dogs show that this is much more increased by giving starch than by giving an equivalent amount of dextrose; the effect is also more prolonged after starch feeding. Older investigations on the question, in which the gaseous interchanges were not examined, are criticised. The original paper must be consulted for full analytical details and methods for calculating results; the main conclusion is that in starch feeding, for every 100 calories of the starch digested, 9·23 calories are produced over and above the inanition figure; for dextrose the figure is only 5·61. When the carbohydrates are given in small quantities, the difference is not noticeable. The low respiratory quotient found is due to the fact that the animals had fasted for two days before the experiment, therefore much of the carbohydrate given would be stored as glycogen, and fat used for combustion. W. D. H.

Carbohydrate Metabolism in Carcinas mænas. E. GRAF VON SCHÖNBORN (*Zeitsch. Biol.*, 1910, **55**, 70—82).—In the crabs investigated, glycogen is found in important amounts; after twenty-five days' inanition, it does not wholly disappear; its amount diminishes at first rapidly, then slowly. On then feeding upon fish, or injecting dextrose, it is again laid on until its amount may reach 2·7% of the body-weight. In the period of chitin formation in the shell, the amount of glycogen is lessened. W. D. H.

The Influence of Carbohydrate and Fat on Protein Metabolism. II. The Effect of Phloridzin Glycosuria. E. Provan Cathcart and M. Ross Taylor (*J. Physiol.*, 1910, **41**, 276—284).—In phloridzin glycosuria, if the carbohydrate in the food is insufficient, there is no excretion of creatine. The carbohydrate cannot be replaced by fat. The output of creatine persists only as long as the glycosuria lasts. There is no apparent causal relationship between acidosis and excretion of creatine. The experiments were made on dogs. W. D. H.

Parenteral Administration of Protein. Kornél von Körösy (*Zeitsch. physiol. Chem.*, 1910, **69**, 313—326).—If a foreign protein is injected into the circulation, it has been held that provided circulation through the alimentary canal is prevented, it passes like a foreign substance into the urine. This is not the case, proteins and proteoses pass into the urine in minimal amounts only, even though the stomach and intestine are extirpated. The injected protein remains therefore in the organism, but whether it is built into the tissues as is protein given enterally is as yet an open question. W. D. H.

Metabolism Experiments with Elastin. Emil Abderhalden and Ernst Ruehl (*Zeitsch. physiol. Chem.*, 1910, **69**, 301—309).—Elastin contains glycine in abundance, leucine, and very little glutamic acid; histidine has been found in so-called hemi-elastin, but tryptophan is absent. In the present research on dogs, elastin was prepared from the neck ligament of the ox; on artificial gastric digestion, hemi-elastin was obtained, but tryptophan was present, although whether this was due to impurities is doubtful. It is badly absorbed, the fæces containing a high percentage of nitrogen; the animals lost weight, and elastin is regarded as inferior to other proteins, although it "spares" them to some extent. It is superior to gelatin. After feeding on elastin, Borchardt (Abstr., 1908, ii, 957) stated that hemi-elastin was discoverable in the blood and urine; these experiments were repeated with a wholly negative result.
W. D. H.

The Assimilation of Natural and Artificial Nourishment. II. Arnold Orgler (*Biochem. Zeitsch.*, 1910, **28**, 359—373).—Puppies of the same litter were fed, some on cow's milk, and some on their mother's milk. They were killed and analysed, some at four and some at six weeks of age. Those fed in the natural way grew more rapidly in weight and strength than the others, and their bodies contained more fat, nitrogen, ash, and calcium. The puppies fed on cow's milk took it freely, and were found with enlarged stomachs after death. The putting on of fat per kilo. of body-weight was more rapid than in those artificially fed. If the figures are reckoned on the fat-free body, the naturally-fed animals show a higher percentage of dry residue, but the nitrogen, ash, and calcium are about equal in the two sets of animals. Dog's milk is richer than cow's milk in protein and ash, and is of greater calorific value. Analytical details are given in full, and compared with those of previous workers. W. D. H.

Distribution of Fluorine in the Human Organs. EMIL ZDAREK (*Zeitsch. physiol. Chem.*, 1910, **69**, 127—137).—Fluorine is widespread in the organs; the quantity is always small, and is relatively greatest in liver, kidneys, and bone. Analyses are given in full. W. D. H.

Detection of Phosphates [in Tissues] with the Molybdate Reagent. RAPHAEL ED. LIESEGANG (*Chem. Zeit.*, 1910, **34**, 1158).—Experiments showing that for histological purposes the application of the ammonium molybdate-nitric acid reagent does not localise the phosphates in tissues. L. DE K.

Incineration of Microtome Sections. RAPHAEL ED. LIESEGANG (*Biochem. Zeitsch.*, 1910, **28**, 413—417).—An attempt was made in the direction of localising the occurrence of certain elements in microscopic section by incinerating them. In the early stages of heating, the blackening indicates the position of carbonaceous material, and here, as also in the later stages of complete incineration, it is still possible to identify the tissue elements, especially in thin sections. Attempts thus to localise iron microchemically were not successful, as the iron is again "masked" as oxide. A similar failure attended attempts to localise iodine in the thyroid, and the various reactions for the detection of phosphorus are either not sufficiently characteristic or worthless. W. D. H.

The Aldehydase in Animal Tissues. FR. BATELLI and LINA STERN (*Biochem. Zeitsch.*, 1910, **29**, 130—151).—By aldehydase is meant the ferment which can convert an aldehyde into a mixture of the corresponding alcohol and acid. In the absence of oxygen the activity can be measured by estimating the amount of acid produced. In the presence of oxygen, certain aldehydes are oxidised further to the acid, although in many tissues the amount of alcohol-oxydase is very small. Acetaldehyde is changed in most tissues more rapidly than salicylaldehyde. Calf's spleen is an exception in this respect. Formaldehyde does not readily undergo the change. The aldehydase is contained in most tissues, especially in the liver of the horse. Preparations containing aldehydase can be produced by precipitation of the tissues by acetone. The ferment acts best in slightly alkaline medium, the optimum temperature being 60°. The rate of reaction was also studied. S. B. S.

Lipoids of the Brain. II. A New Method for the Preparation of the Galactosides and of Sphingomyelin. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1910, 1—11; *J. Physiol.*, **41**. Compare Abstr., 1909, i, 282).—Cholesterol is first removed by extraction with cold acetone, and then lecithin and kephalin by extraction with ether or light petroleum; the residue is then reduced to a fine powder, and extracted with cold pyridine; the extract is reddish in colour, and shows an absorption spectrum similar to that of hæmochromogen; it is poured into acetone, and a bulky precipitate of impure galactosides (phrenosin and kerasin) is thus

obtained; these can be separated by fractional crystallisation from 85% alcohol at 30° and 0°, and subsequently purified by several methods. If the residue is now extracted with warm pyridine (40—45°), sphingomyelin is dissolved out, which is precipitated by cooling to room temperature, and subsequently purified. Molisch's reaction is a very delicate one for the detection of the galactosides.

W. D. H.

Lipoids. XIII. Composition of the Spinal Cord. SIGMUND FRÄNKEL and LUDWIG DIMITZ (*Biochem. Zeitsch.*, 1910, **28**, 295—319).—The spinal cord contains 74% of water, 18% of lipoids (being the part of the central nervous system richest in these substances), and 8% of the proteins described by Halliburton, who, however, put the percentage higher. The amount of water increases with age. The cholesterol present (4%) is in the free condition, as in the brain. A great part of the unsaturated phosphatides consists of kephalin; the saturated lipoids are only present to the extent of 1·5%.

W. D. H.

Union of Certain Poisons with Cardiac Muscle. HORACE M. VERNON (*J. Physiol.*, 1910, **41**, 194—232).—Alcohol added to Ringer's fluid perfused through the tortoise heart lessens the amplitude of the heart's contraction; after about twelve minutes, the amplitude remains at a small, but constant, level; this effect is removed by perfusing with pure Ringer's solution. Ether and chloroform act in the same way, but smaller doses are required to produce the same effect as alcohol; their action is also reversible; the concentration of the poison does not affect this result. Hydrocyanic acid acts in the same way, except that the effect is not proportional to the concentration; greater concentrations than 0·01% permanently injure the heart. Probably the same amount of poison is united to the cardiac substance in spite of variations in its concentration. Sodium fluoride acts somewhat in the same way; on washing out with pure saline, the ventricle usually shows one to three huge waves of tonus oscillation. Formaldehyde very slowly reduces the contractions to a constant level, proportional to the concentration (0·001 to 0·008%), and recovery on washing out is very slow. Alcohol, ether, and chloroform slow, and may stop, the heart. Formaldehyde, hydrocyanic acid, and sodium fluoride seldom stopped the heart absolutely, and in many experiments did not affect its rate. Hearts depressed in vitality are more sensitive to the action of poisons, especially of chloroform. It is regarded as probable that alcohol, ether, and chloroform enter into a loose union with the colloidal lipoids or other constituents of the cardiac tissue by means of molecular valencies, whilst hydrogen cyanide, sodium fluoride, and formaldehyde enter into definite chemical combination by means of atomic valencies.

W. D. H.

Autolysis. WALTHER LINDEMANN (*Zeitsch. Biol.*, 1910, **55**, 36—52).—Autolysis in the livers of rabbits, cats, and dogs was studied under aseptic conditions. Protein hydrolysis, acid formation, and development of gas occur only if the organs are kept at 37°.

Carbon dioxide and hydrogen appear in most variable proportions; hydrogen may be absent in the case of the rabbit. No constant relationship was found between the production of carbon dioxide and volatile fatty acids; this is against a fatty acid fermentation of carbohydrate. The possibility of the acids arising from protein was shown by the occurrence of de-amidation. W. D. H.

The Behaviour of the Fat of Organs in Autolysis, and on Preservation Under Aseptic Conditions. KOHSHI OHTA (*Biochem. Zeitsch.*, 1910, **29**, 1—12).—To investigate the question as to whether fat can be formed from proteins, liver and heart muscular tissues were preserved in the cold and at 37—40° with chloroform water, and the amounts of fatty acids in the unchanged tissues, together with the cholesterol in the changed and unchanged tissues, were estimated. It was found that there was no increase of fatty acid produced under any conditions in the liver tissue, whereas the results in the heart muscular tissue were irregular, probably owing to the want of homogeneity in the original tissue. Owing to the small quantities of cholesterol, and the consequent uncertainties due to experimental error, no conclusion could be drawn as to whether this substance increases in amount or not. S. B. S.

The Oxidation Processes of Lipoids of the Spinal Column. E. SIGNORELLI (*Biochem. Zeitsch.*, 1910, **29**, 25—30).—It has already been shown by Scaffidi that the nervous tissue, especially during degeneration, absorbs relatively large amounts of oxygen. The author now shows that the lipoids prepared from fresh nervous tissue also absorb oxygen, owing probably to the presence of unsaturated lipoids. The experiments were carried out by means of a microspirometer. S. B. S.

The Amount of Erepsin in Blood-free Organs. OTTO COHNHEIM and DIMITRI PLETNEFF (*Zeitsch. physiol. Chem.*, 1910, **69**, 108—112).—Vernon found the duodenal mucous membrane to be richest in a peptolytic enzyme (erepsin), whilst among the organs, the kidneys possessed most and the blood least. He determined this colorimetrically by the biuret test. Abderhalden uses the splitting off of tyrosine from glycyl-tyrosine as his test for such enzymes. In the present research a slight modification of Vernon's method was employed to test the presence of erepsin in cat's organs (kidneys, lungs, muscles); the results confirm those of Vernon; the organs were freed from blood by Ringer's solution. Erepsin, or, at any rate, a peptolytic enzyme, is therefore present in the tissue cells independently of the blood. W. D. H.

The Isolated Kidney. The Influence of Pulse Pressure upon Renal Function. DONALD R. HOOKER (*Amer. J. Physiol.*, 1910, **27**, 24—44).—A perfusion apparatus for the dog's kidney is described, which yields a pulsatile wave of pressure similar to the normal pulse. The amount of urinary filtrate and the rate of blood flow vary directly as the magnitude of the pulse pressure; the amount of

protein varies inversely as this magnitude; in all cases the mean perfusion pressure was constant. W. D. H.

The Cortex of the Suprarenal Body. K. KAWASHIMA (*Biochem. Zeitsch.*, 1910, **28**, 332—339).—Extracts of the cortical region of the horse's suprarenal contain no enzyme capable of destroying adrenaline. Small quantities of adrenaline or a related substance are present. W. D. H.

The Behaviour of the Chromaffine Substance of the Suprarenal Body in Hunger and Under the Influence of Potassium Iodide. F. VENULET and G. DMITROWSKY (*Arch. exp. Path. Pharm.*, 1910, **63**, 460—464).—In inanition, the chromaffine substance of the suprarenal is diminished; administration of adrenaline under these conditions prolongs life. Potassium iodide is inhibitory towards the secretion of adrenaline, and this in addition to its depressor action is considered to explain its therapeutic use in arteriosclerosis. W. D. H.

The Peptide-splitting Enzyme of Ovaries. A. KOBLENCK and WALTHER LÖB (*Biochem. Zeitsch.*, 1910, **29**, 102—103).—The ovaries of rabbits and pigs contain an enzyme capable of hydrolysing glycyl-tryptophan. S. B. S.

Changes in the Skin following the Application of Local Anæsthetics. I. Ethyl Chloride. SHEPHERD IVORY FRANZ and WILLIAM C. RUEDIGER (*Amer. J. Physiol.*, 1910, **27**, 45—59).—Ethyl chloride is an anæsthetic and analgesic; analgesia (insensibility to pain) being the more persistent. This is in favour of the view that pain is a sensation subserved by nerve- and end-organs distinct from those concerned in tactile impressions. Sensations of temperature are dulled. W. D. H.

Laxatives and the Calcium of the Intestine. RICHARD CHIARI (*Arch. exp. Path. Pharm.*, 1910, **63**, 434—440).—Saline purgatives which precipitate calcium ions increase the calcium in the intestinal wall, and calomel and alkaloids lessen it. W. D. H.

Is the Stoppage of Rhythmic Contractions in a Solution of Pure Sodium Chloride Due to Increased Rate of Oxidation? JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1910, **28**, 350—352).—Direct measurements show that there is no increased absorption of oxygen due to the presence of sodium chloride in solutions containing organisms which undergo rhythmic contractions, so that the question in the title is answered in the negative. The retarding action of sodium chloride on the rhythmic contractions of *Medusa* is not removed by addition of sodium cyanide. G. S.

Production of Light by the Firefly. JOSEPH H. KASTLE and F. ALEX. McDERMOTT (*Amer. J. Physiol.*, 1910, **27**, 122—151).—Three things are concerned in the production of light by living organisms: the

photogenic substance, water, and oxygen. The first is characterised by extreme irritability, but its composition is unknown. Chemical stimuli, especially ether, chloroform, carbon disulphide, carbon tetrachloride, nitrobenzene, and nitrites of certain metals, cause a continuous formation of light in the firefly, whereas normally light emission is intermittent, resembling a series of luminous explosions. Of the substances tried, sulphur dioxide is the most toxic. Great diminution of atmospheric pressure causes emission of light in the living animal and in the detached luminous organ. The photogenic material can be dried in a vacuum, and retains its power to emit light when moistened for at least thirteen months. W. D. H.

The Secretion of the Infundibular Lobe of the Pituitary Body and its Presence in Cerebrospinal Fluid. HARVEY CUSHING and EMIL GOETSCH (*Amer. J. Physiol.*, 1910, **27**, 60—86).—The view that the active principle of this gland is secreted into the ventricular cavity is supported by the discovery that the cerebrospinal fluid contains a substance which acts on blood-pressure like "pituitin." This can be demonstrated in concentrated specimens of the fluid. Pituitin is believed to be a product of the hyaline substance of the *pars nervosa.* W. D. H.

The Reducing Properties of Milk, Liver, and Yeast. LEOPOLD ROSENTHALER (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 448—453).—From the results of experiments in which the action of milk on phenylglyoxylic acid was investigated, the author comes to the conclusion that the reducing power of milk on such substances as the methylene-blue of Schardinger's reagent (Abstr., 1903, ii, 190), etc., is due to bacterial action, and not to that of enzymes. The analogous actions of liver and yeast are due to the same cause. W. P. S.

Aporrhegma. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, **69**, 265—272).—The name aporrhegma is given to the decomposition products of protein amino-acids formed by physiological processes in the living plant or animal, and includes the common ptomaines and acids formed by putrefaction.

Attention is drawn to the fact that although methylated nitrogenous compounds are present in large quantities in vegetable tissues, they are rarely met with in animal tissues. Methylated glycine has been extracted from the muscles of *Crangon vulgaris*, *Astacus fluviatilis*, and *Acanthias vulgaris*, but does not appear to be present in the muscle of mammalians. It is suggested that in warm-blooded animals the nitrogenous products are got rid of by processes of oxidation, but that in plants and cold-blooded animals they are removed by means of complete methylation. Methylation can occur in the case of warm-blooded animals when oxidation is stopped to an appreciable extent, for example, in cases of phosphorus poisoning.

A list of aporrhegma and their corresponding amino-acids is given, and also a list of methylated aporrhegma. J. J. S.

A New Aporrhegma Prepared by Bacterial Agencies. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1910, **69**, 273—281. Compare this vol., i, 419).—Lysine mixed with Witte's peptone and dextrose

undergoes bacterial putrefaction in the presence of a small amount of putrefying pancreas, and, after nineteen days at 36°, yields appreciable amounts of pentamethylenediamine, which can be isolated as the picrate or aurichloride. A small amount of a product which yields a readily soluble platinichloride is also formed.

Arginine under similar conditions yields tetramethylenediamine and δ-aminovaleric acid, but not agmatine, and glutamic acid yields γ-aminobutyric acid (compare Schotten, Abstr., 1883, 813; Gabriel, *ibid.*, 1890, 360), by the elimination of carbon dioxide.

It has not been found possible to isolate methylamine and ethylamine from the products formed by the action of anaerobic bacteria on glycine and alanine. J. J. S.

A Methylated Aporrhegma from Animal Tissues. R. ENGELAND and FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, **69**, 282—285).—The γ-aminobutyric acid obtained from glutamic acid (compare Ackermann, preceding abstract) is identical with the synthetical acid. The *aurichloride*, $C_4H_9O_2N,HAuCl_4$, crystallises in glistening plates, m. p. 138°.

When methylated, the γ-amino-acid yields a product from which an aurichloride, $C_7H_{16}O_2N,HAuCl_4$, can be obtained, identical with the aurichloride, m. p. 203°, from γ-butyrobetaine chloride isolated by Takeda (this vol., ii, 797) from the urine of dogs poisoned by phosphorus. The *platinichloride* of the *ethyl* ester,

$$(C_6H_{15}N\cdot CO_2Et)_2PtCl_6,$$

has m. p. 222° (decomp.). The occurrence of this betaine in substances of animal origin is due to the decomposition of glutamic acid and the methylation of the γ-aminobutyric acid. The α-hydroxy-γ-butyrobetaine formed in muscle extract is probably the first oxidation product of γ-butyrobetaine. J. J. S.

Distribution of Nitrogen in the Intestinal Excreta. HENRI LABBÉ (*Compt. rend.*, 1910, **151**, 822—824).—Normal human fæces were extracted successively with ether, benzene, aqueous sodium carbonate, and glacial acetic acid. Nitrogen was determined in the original fæces, in each extract, and in the insoluble residue. The results are given in tabular form. The benzene extract appeared to contain the substances of the lecithin type, whilst the alkaline extract probably contained the amino-acids. W. O. W.

The Secretion of Urine. JOSEPH BARCROFT and HERMANN STRAUB (*J. Physiol.*, 1910, **41**, 145—167).—The diuretics studied fall into two groups: (1) those which produce urine without alteration in the gaseous exchange of the kidney (Ringer's solution, and sodium chloride in hyper- and hypo-tonic solutions); (2) those which cause increased gaseous exchange (urea, caffeine, sodium sulphate, phloridzin). In the case of urea and caffeine there is a definite poisoning action, as shown by subsequent depression of the gaseous exchange. The distinctive features of the urine produced by the second class are attained by a process of secretion on the part of the tubules, and not by a process of re-absorption. After poisoning the cells by corrosive

sublimate or by the diuretics of the second class, a flow of urine can still be produced by the first class of diuretics; the urine so produced appears to be isotonic with the blood-serum. Clamping the kidney vessels for fifteen minutes after washing out with Ringer's solution does not abolish its power of secretion. The special interest of the research is the action of diuretics of the first class, and these produce urine independently of secretory activity (as judged by the absence of increased metabolism), and so their action must be attributed to mechanical filtration; the experimental methods adopted were such that changes in rate of blood flow or of blood pressure could be excluded. The proteins of the blood-plasma in virtue of their osmotic pressure would attract water into the blood; the capillary pressure would drive water into the urine. Suppose, for instance, that the capillary pressure is equal to 27 mm. of mercury, and that the osmotic pressure of the proteins is a little lower, say, 25, as it probably is in normal circumstances, then the available pressure for filtration would be 2 mm. If the amount of protein in the blood-plasma were reduced to half, the osmotic pressure will be reduced to 12·5, and the available filtering pressure is thus 14·5, or seven-fold increase, and diuresis will occur. This argument was justified by testing it as follows: the animal was bled very considerably, and the blood replaced by Ringer's solution containing blood corpuscles in suspension; the diuresis so produced was very considerable, although the blood-pressure was very low, and this was attended with no increase in the gaseous exchange. W. D. H.

A Comparison of the Total Nitrogen Excretion of either Kidney in Normal Individuals. THEODORE B. BARRINGER, jun., and BENJ. S. BARRINGER (*Amer. J. Physiol.*, 1910, **27**, 119—121).—Observations were made on eleven young men. One ureter was catheterised, a bladder catheter collecting the urine from the other kidney. Details are given of the quantity of urine, in periods varying from twenty to one hundred and twenty minutes, secreted by each kidney, also the total nitrogen, and the sum of urea and ammonia nitrogen. The differences noted are usually small. W. D. H.

The Excretion of Parenterally Administered Creatine in Mammals. CORNELIS A. PEKELHARING and C. J. C. VAN HOOGENHUYZE (*Zeitsch. physiol. Chem.*, 1910, **69**, 395—407).—Injection of creatine into the blood-stream of rabbits, led to the result that this substance is, in part, decomposed in the body, and partly excreted as creatinine by the kidneys. The liver appears to be specially concerned in its destruction and in its conversion into creatinine. W. D. H.

The Excretion of Organically United Phosphorus in Urine. KURA KONDO (*Biochem. Zeitsch.*, 1910, **28**, 200—207.).—Previous work on the organic phosphorus compounds of the urine in health and disease have shown that they are increased by the administration of glycerol-phosphates and lecithin. In the present research, a dog was fed on horse-flesh and lard, and then to this were added for two or three days' periods, brain, casein, and thymus. On normal days the

organic phosphorus in percentage parts of total phosphorus averaged 2·7, on the brain days 3·3, and on the casein and thymus days 1·5. W. D. H.

The Influence of the Fat of the Food Ingested on the Excretion of the Acetone Substances. GUNNAR FORSSNER (*Chem. Zentr.*, 1909, ii, 1759; from *Skand. Arch. Physiol.*, 1909, **22**, 349—392).—The excretion of acetone and β-hydroxybutyric acid depends on the food ingested. After meals there is a regular increase in the excretion of acetone substances, and the missing of a meal causes a distinct change in the regular curve representing the excretion, and a marked diminution in the amounts excreted. The excretion depends on the fat ingested; no difference could be detected between the action of the higher fatty acids (lard, etc.) and the lower fatty acids (butter). When the store of glycogen in the body had diminished, relatively small quantities of fat caused acidosis, similar to that of severe diabetes. S. B. S.

The Influence of Muscular Work on the Excretion of Acetone Substances, with Diets Poor in Carbohydrates. GUNNAR FORSSNER (*Chem. Zentr.*, 1909, ii, 1760; from *Skand. Arch. Physiol.*, 1909, **22**, 393—406).—On different days, certain amounts of muscular work were performed (marching), which were in the ratios of 1, 2, 3, and 4. The average diet consisted of 111·7 grams protein, 239 grams fat, and 59·4 grams carbohydrates. Muscular work was found to diminish the body reserve of carbohydrates, which are concerned in the formation of acetone substances. This diminution was, however, only proportional to the amount of work performed within certain limits. The maximal action under the condition of experiments was attained by a forced march lasting for two to thirty-six minutes. S. B. S.

Melanuria. HANS EPPINGER (*Biochem. Zeitsch.*, 1910, **28**, 181—192). —The origin of the black pigment which occurs in certain malignant tumours and passes into the urine is obscure, and the suggestion that it originates from tyrosine by the action of a tyrosinase is due to experiments *in vitro* only. The present research shows that this pigment (melanin) originates from tryptophan. By feeding with tryptophan, the excretion of the pigment is increased three-fold, whereas tyrosine and phenylalanine, the parent substances of homogentisic acid, have no effect. The urine is sometimes darkly coloured when passed, sometimes the darkening comes on after exposure to the air, but in all cases of melanotic tumour, it appears on the addition of oxidising agents; the material in the urine is then not melanin, but melanogen. This can be precipitated from the urine with sulphuric acid and mercuric sulphate, and can then be dissolved out from the precipitate by a method which is described in full, and finally obtained in crystalline form. These crystals show all the colour and other reactions of melanogen as contained in the original urine. The following formula was calculated from its percentage composition: $C_6H_{12}O_4N_2S$, and it is regarded provisionally as a hydroxy-*N*-methylpyrollidinecarboxylic acid in the form of an ethereal sulphate. Another

substance was separated from the same urine; it is probably related to the first, but this requires further investigation. W. D. H.

Acapnia and Shock. VII. Failure of the Circulation. YANDELL HENDERSON (*Amer. J. Physiol.*, 1910, **27**, 152—176. Compare this vol., ii, 622).—The essential factor in the circulation in shock is not heart failure, but failure of the veno-pressor mechanism, which consists, in part, of the tonus of the tissues and, in part, of osmotic processes. Tonus is largely dependent on the carbon dioxide they contain, and when the tension of carbon dioxide (regulated by the respiratory centre) is diminished in acapnia, the blood stagnates in the venous reservoirs. Acapnia upsets osmotic processes; water passes out of the blood into the tissues, and is ultimately followed by tissue asphyxia and acidosis. W. D. H.

The Fundamental Constituents of Tumour Cells. EMIL ABDERHALDEN and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1910, **69**, 66—71).—Tyrosine, glutamic acid, and glycine were estimated in the cell proteins derived from various malignant tumours. The different kinds of tumours all yielded the three amino-acids in approximately the same proportion. W. D. H.

The Theory of the Wassermann Reaction. E. GATZ and R. INABA (*Biochem. Zeitsch.*, 1910, **28**, 374—391).—Sachs and Rondoni have shown that dilution of the alcoholic extract of the syphilitic liver with salt solution causes a cloudiness, which varies as the dilution is effected slowly or rapidly. The manner of dilution influences the power of the extract in uniting with complement, and they explain this as due to a physical cause, namely, the size of the particles in suspension. There is an undoubted alteration as Sachs and Rondoni described, and this disappears on cooling; moreover, the difference does not run parallel to the change in hæmolytic power; the latter, however, does not remain unaltered. Sharper results are obtained in extracts diluted slowly, and those who use the Wassermann reaction for the biological detection of syphilis must recognise the importance of this factor. It appears doubtful if the explanation is wholly physical. W. D. H.

Serological Studies with the Help of the Optical Method. XI. Parenteral Administration of Carbohydrates. EMIL ABDERHALDEN and GEORG KAPFBERGER (*Zeitsch. physiol. Chem.*, 1910, **69**, 23—49).—Sucrose injected either into the blood or subcutaneously is inverted in the blood, but great differences are seen in different animals. Lactose is also affected, but not raffinose. After the injection of lactose, dog's serum or plasma inverts sucrose and lactose, but not raffinose. The action of the these fluids on the two disaccharides is noticeable seven to eight hours after a subcutaneous injection of either, and lasts at least fourteen days. Whether the urine has the same power has not yet been investigated. The agent in the blood that acts on the sugars, dialyses into distilled water. A temperature of 60° destroys the power, and of 4° lessens it. W. D. H.

The Influence of Pharmacological Agents on Oxidation in the Organism. JULIUS BAER and WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1910, **63**, 441—459).—The importance of oxidation as a source of energy, and the way in which body functions are influenced by drugs acting on oxidation processes are well illustrated by recent work on narcosis. In the present research, the point investigated was acetone formation in the liver perfused with various drugs, namely, potassium cyanide, chloral hydrate, trichloroacetic acid, dimethylbarbituric acid or ethylbarbituric acid (veronal), salicylic acid, salicylaldehyde, saligenin, *p*-hydroxybenzoic acid and aldehyde, and *m*-hydroxybenzoic acid and aldehyde. All of these inhibit acetone formation in varying degrees, but the figures given show that the variation is not proportional to their effect on oxidation; indeed, some increase oxidative processes. In the oxidation of butyric and hydroxybutyric acids in the liver, two different processes or factors have therefore to be dealt with. W. D. H.

Behaviour of Phloridzin after Extirpation of the Kidneys. ERICH LESCHKE. **Answer to the Preceding.** KARL GLAESSNER and ERNST P. PICK (*Pflüger's Archiv*, 1910, **135**, 171—175, 176. Compare this vol., ii, 530).—Polemical. Both sides maintain their original position. W. D. H.

Quantitative Investigations on the Chemistry of Strophanthin Action. WALTHER STRAUB (*Biochem. Zeitsch.*, 1910, **28**, 392—407).—Alkaloids which act on certain organs, such as the heart, can be washed out and re-obtained in the washings, and their action is thus reversible. This is not the case with the digitalis glucoside. Strophanthin is in this relation similar to alkaloids, and its action is largely reversible. Tested on a frog's heart by perfusion, the reaction is proportional to the concentration of the drug, and there is probably a chemical action between the cell constituents and the glucoside, although very little of the latter is used in the combination or interaction, and there is no storage in the heart muscle. W. D. H.

The Systolic and Diastolic Heart-Action of Strophanthin. N. WERSCHININ (*Arch. exp. Path. Pharm.*, 1910, **63**, 386—404).—This drug in Ringer's solution applied to the exterior or interior of the frog's heart leads in small concentrations to diastolic stoppage, in medium doses to systolic stoppage, and in high concentrations to diastolic stoppage and paralysis. Mixed with blood-serum, the toxic power is much increased. This is, in part, due to the lipoids present, and lecithin exerts a similar action, but the effect in producing systolic stoppage appears to be specially due to the salts of the serum, particularly those of calcium, but calcium salts only exert this influence when applied endocardially. W. D. H.

The Action of Strophanthin on the Blood-Vessels. MAX KASZTAN (*Arch. exp. Path. Pharm.*, 1910, **63**, 405—423).—The effect of members of the digitalis family in raising arterial pressure is, in part, due to vaso-constriction, and large doses will soon contract the

kidney blood-vessels and lessen the flow of urine. The present research specially takes up this point, and the organs of cats, rabbits, and dogs were perfused with strophanthin in Ringer's solution. Solutions of one or more per million constrict the blood-vessels of kidney and intestine; concentrations below this dilate them, but here a difference between the kidney and intestine is noted, for smaller concentrations, which constrict the intestinal, will still dilate the kidney blood-vessels. W. D. H.

[Physiological] Action of Atropine, Pilocarpine, and Physostigmine. ARTHUR R. CUSHNY (*J. Physiol.*, 1910, **41**, 233—245).—Pilocarpine causes contraction or inhibition of the cat's uterus, according to the condition of the organ, in this resembling the effects of adrenaline or hypogastric stimulation. Its contractor action is antagonised by ergotoxine, as is that of adrenaline or electric stimulation. It differs from adrenaline in being antagonised completely by atropine whether it contracts or inhibits the uterus. Physostigmine contracts the uterus, and is antagonised by atropine. It is suggested that pilocarpine and atropine act on receptive substances associated with the nerve impulse path to the uterus, but do not lie actually on this path. Physostigmine may probably affect the receptors associated with the augmentor path only. In the case of other abdominal organs, the same explanation is regarded as tenable, whilst, in other cases, the receptive substances are regarded as lying on the impulse path, since this is interrupted by atropine.
W. D. H.

The Behaviour of Morphine in the Frog. BRONISLAW FRENKEL (*Arch. exp. Path. Pharm.*, 1910, **63**, 331—340).—Most previous workers on morphine have employed warm-blooded animals. Frogs differ from these in the prolonged period of primary excitation, culminating in tetanus, and in manifesting no immunity. Morphine is retained for a long time in the frog's body; after eight days it is, however, all eliminated, mainly by the alimentary tract, from which 65% of the amount given is recoverable; comparatively little (10%) is destroyed in the body. None is found in the central nervous system, but the liver, and next to that the muscles, contain most. The destruction is increased by an elevation of body-temperature and of oxygen tension. W. D. H.

Influence of the Concentration of Hydroxyl Ions in a Sodium Chloride Solution on the Relative Anti-Toxic Action of Potassium and Calcium. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, **28**, 176—180).—The poisonous action of sodium chloride on the developing fertilised eggs of the sea-urchin is neutralised to a greater extent by potassium than by calcium in neutral or slightly acid solution; in alkaline solution, on the other hand, calcium is more effective than potassium. In all cases the effect of a mixture of potassium and calcium is greater than the sum of the separate effects. Addition of alkali to a mixture of potassium and sodium chloride increases the poisonous action, whereas alkali renders a mixture of sodium and calcium chloride less poisonous. G. S.

Why Does Sodium Cyanide Diminish the Poisonous Action of Sodium Chloride on Sea-Urchin's Eggs? JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1910, **28**, 340—349).—Warburg (this vol., ii, 628) accounts for the poisonous action of sodium chloride on sea-urchin's eggs on the assumption that it increases the oxidation processes to such an extent that the egg is disadvantageously affected, the favouring effect of the calcium being due to its property of bringing back the rate of oxidation to the normal value. The authors have determined the amount of oxygen used up when the eggs develop in different solutions, and show that in sodium chloride solution there is no increase, but if anything a decrease, in the amount of oxygen absorbed. Warburg's observation that more oxygen is used up in a given time in a solution containing sodium chloride and cyanide than in the same solution with the addition of calcium, is confirmed, but no final explanation is advanced. The anti-toxic effect of sodium cyanide in a solution containing sodium chloride is ascribed to the former substance retarding the development of the egg or the oxidation changes accompanying development. G. S.

The Inhibition of the Toxic Action of Certain Poisons on the Eggs of Sea-Urchins Due to Depression of Oxidation in the Eggs. JACQUES LOEB (*Biochem. Zeitsch.*, 1910, **29**, 80—95).—It was found that the stoppage of oxidation in the eggs, either by sodium cyanide or by driving out oxygen from the artificial sea-water by hydrogen, inhibited the toxic action of the following classes of substances: (1) Neutral salt solutions; (2) sugar solutions; (3) hyper- and hypo-tonic solutions; (4) narcotics (chloral hydrate, phenylurethane, chloroform, and alcohol). This action of deficient oxidation cannot be due to inhibition of the bifurcation process, for it inhibits the toxic action of substances like chloral hydrate, which themselves inhibit the bifurcation of the egg. S. B. S.

The Removal of the Poisonous Effects of Hydrocyanic Acid by Substances which Split off Sulphur. JOSEF HEBTING (*Biochem. Zeitsch.*, 1910, **28**, 208—212).—Lang found that hydrocyanic acid compounds led to the excretion of thiocyanates, and in minced organs the change of potassium cyanide into thiocyanate also occurs, the sulphur arising probably from the cystine of protein. He further showed that various sulphur compounds protect the organism against the poisonous effects of hydrocyanic acid. Reid Hunt and others have confirmed this. In the present research on rabbits, the antidotes investigated were sodium tetrathionate, cystine, β-thiolactic acid, and α- and β-dithiodilactylic acids, and Lovén's trithio-compound, $C_6H_{10}O_4S_3$. All were protective in some degree, but none reach thiosulphate in efficiency. W. D. H.

The Supposed Immunity of Toads to their own Poison (Secretion of Skin Glands). HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1910, **63**, 374—385).—It has been generally stated that toads, like snakes, are immune to their own poison. The cutaneous secretion

of toads contains several active constituents, namely, a hæmolysin called phrynolysin, and two substances, bufonin, similar to cholesterol, and an easily soluble substance, bufotalin. The last two substances produce the main toxic symptom, namely, a digitalis-like action on the heart. It is shown in the present research that the hearts of frogs are easily affected by the toad's poison, stoppage and systolic contracture being produced; the same occurs also in the toad's heart. This action is to a great extent annulled by previous treatment of the secretion with cholesterol. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Spontaneous Ignition of Coal. ERNST GALLE (*Centr. Bakt. Par.*, 1910, ii, 28, 461—473).—The bacteriological examination of five kinds of coal showed the presence of seven kinds of spores, of which three were identified as *Bacillus subtilis*, *B. mesentericus*, and a kind of *Sarcina*. The spores develop at the ordinary temperature and without air, and non-sterilised coal, moistened with tap-water, gave in one experiment a luxuriant growth of bacteria.

Further experiments on the production of gas from coal by the action of bacteria showed that four of the seven microbes produce inflammable gas, about three-fourths methane, about one-fifth carbon dioxide, with small amounts of carbon monoxide. The bacterial action was found to result in a rise of temperature, the greatest effect being produced by *B. pseudosubtilis* (1·9°). Finally, it is shown that coal which has been subjected to the action of the bacteria ignites at a lower temperature.

The conclusion is drawn that whilst bacteria are not the direct cause of the spontaneous ignition of coal, they may play an important part in the production of conditions which result in ignition.

N. H. J. M.

The Destruction of Gelatin by Micrococcus prodigiosus. P. MESERNITZKY (*Biochem. Zeitsch.*, 1910, 29, 104—125).—*Micrococcus prodigiosus* contains an enzyme which is capable of liquefying gelatin, and can be detected in culture media after some days. It is very heat-stable. The products of the action of the organism on gelatin were also investigated, and the amounts of nitrogenous matter precipitable by tannin solutions after varying intervals of culture were estimated. In addition to these peptides, crystalline substances were also produced, of which only glycine was identified with certainty. Probably leucine and proline were also produced.

S. B. S.

Action of Nitrates in Alcoholic Fermentation. AUGUSTE FERNBACH and A. LANZENBERG (*Compt. rend.*, 1910, 151, 726—729).—It has been held that the presence of nitrates during alcoholic fermen-

tation is harmful, owing to the toxicity of these substances towards yeast. This view, based on the experiments of Mayer (1869) and of Dubrunfaut (*Compt. rend.*, 1871, **73**, 263), is now shown to be incorrect. Potassium nitrate has a slightly inhibitory effect when present to the extent of 0·1%, but in concentrations exceeding this, up to 2%, it strongly stimulates the production of alcohol.

Experiments were also conducted on zymase with similar results; the amount of carbon dioxide produced was found to increase to a marked extent when the salt was present in 0·5—4% solution. The optimum concentration varied with the nature of the yeast from which the enzyme was prepared. It was found, however, that the multiplication of yeast cells is checked by nitrates, especially in the more concentrated solutions. W. O. W.

Influence of Nitrates on Alcoholic Ferments. E. KAYSER (*Compt. rend.*, 1910, **151**, 816—817. Compare Abstr., 1907, ii, 288, 383, 903; Fernbach and Lanzenberg, preceding abstract).—Manganese nitrate is even more active than the alkali nitrates in promoting alcoholic fermentation. The optimum dose of this salt varies with the nature of the yeast. W. O. W.

Influence of Environment on Enzymic Action. FREDERICK W. PAVY and HUBERT W. BYWATERS (*J. Physiol.*, 1910, **41**, 168—193).—The inverting power of an aqueous extract of yeast is increased ten- to fifteen-fold by the addition of a boiled extract of yeast. This is attributed to the acidity of the boiled extract, for the same results can be obtained by substituting acetic acid for the boiled extract. If yeast cells are used, acetic acid has the same activating effect up to a certain optimum point, after which addition of acid diminishes the inverting power. After desiccation, treatment with alcohol, or grinding with kieselguhr, yeast yields an aqueous extract with enhanced enzymic power, which acid fails almost entirely to increase further. The activity produced by acid can be removed by the addition of alkali. The diastatic enzyme of the oyster is influenced by boiled oyster extract and by acetic acid in the same way, but not to so great an extent. The addition of acid, not only increases the amount of reducing substance, but also increases its reducing power. The post-mortem production of sugar in the liver can be checked by an alkaline injection, and subsequently the production of sugar can be increased by rising amounts of acid until an optimum is reached. The dried or coagulated liver behaves to acid and alkali like the fresh organ. The post-mortem production of sugar and of acid by the liver runs on parallel lines, and the acidity so produced is regarded as the governing factor for sugar formation. Fluorides restrain the formation of both acid and sugar. W. D. H.

The Kinetics of Toxic Action of Dissolved Substances. I. The Influence of Concentration. THEODOR PAUL, GUSTAV BIRSTEIN, and ANTON REUSS (*Biochem. Zeitsch*, 1910, **29**, 202—248).—The disinfecting action, determined by means of the Krönig-Paul garnet method, of various acids on different bacteria was estimated. Acetic

and *n*-butyric acids were found to be more powerful disinfectants than hydrochloric acid in isohydric solutions. The disinfection constant of hydrochloric acid in $N/25$—$N/150$ solutions was found to be approximately proportional to the square-root of the concentration of the acid. For butyric acid in concentrations $N/6{\cdot}6$—$N/26$, it was proportional to the square of the concentration, or for acetic acid in concentrations $N/2$—$N/31$, the disinfection rate was approximately proportional to the concentration itself. The relationship between the disinfecting action and concentration of a substance can be expressed by the general equation: $K = A.C^B$, where K = constant of disinfection rate, C = concentration, and A and B are constants. The exponent B is the characteristic constant for any particular disinfectant. S. B. S.

The Kinetics of Toxic Action of Dissolved Substances. II. The Influence of Neutral Salts and Temperature on the Disinfection Rate of Acids. THEODOR PAUL, GUSTAV BIRSTEIN, and ANTON REUSS (*Biochem. Zeitsch.*, 1910, **29**, 249—278).—Certain inorganic substances increase the disinfection rate of inorganic acids without themselves acting as disinfectants; an aqueous solution with equivalent quantities of the acid HX, and the salt MX_2, has approximately the same disinfection rate as an acid HX_2. The disinfection rates of acid-salt mixtures with different contents in salt are approximately the same as those of the salts having the corresponding concentration. The temperature-coefficients of the disinfection rates were also determined. S. B. S.

Catalase of Moulds. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1910, **32**, 1357—1361).—A study of various species of *Penicillium* and *Aspergillus* has shown that these moulds contain catalase. When the mycelium first appears on the surface of the culture-medium, it contains a very active catalase, but, after about fifteen days, the quantity of this enzyme in the cells of the fungus gradually decreases, whilst that in the medium steadily increases. The means by which this passage of the catalase from the mould into the medium is effected cannot at present be explained, but it seems probable that some of the cells of the fungus undergo disintegration or suffer a loss of vitality, thus allowing the enzyme to diffuse or to be mechanically discharged into the medium. E. G.

Formation of Hydrogen Cyanide in the Germination of Seeds. CIRO RAVENNA and M. ZAMORANI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 356—361).—Although the seeds of *Sorghum vulgare* do not contain hydrogen cyanide, yet the distillate from them when germinating always yields that substance. This is the case whether germination takes place in the dark or in light, and the amount found increases to a certain limit (0·08% of the weight of the seeds), then decreases. The seeds of *Linum usitatissimum*, which contain hydrogen cyanide (0·027%), behave similarly, but the maximum amount is greater (0·5%). It is suggested that carbon dioxide or carbohydrates are concerned in the formation of the acid. Less was produced (in some experiments) in the absence of carbon dioxide,

whilst seedlings grown in the dark and supplied with dextrose produced more than similar etiolated plants not so treated.

R. V. S.

The Elective Rôle of the Root in the Absorption of Salts. JEAN DE RUFZ DE LAVISON (*Compt. rend.*, 1910, **151**, 675—677).—The rate of absorption of sodium, potassium, and calcium chloride from aqueous solutions by the cut stems and roots of plants has been determined. It was found in the case of the haricot that sodium chloride was not absorbed by the roots, whilst considerable quantities passed into the stem. The latter absorbed all the salts presented to it with equal facility, whilst the roots showed a marked selective action.

W. O. W.

Cryoscopic Determination of the Osmotic Pressures of Some Plant Organs. W. R. GELSTON ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1910, **12**, 463—469).—Records are given of measurements of the osmotic pressure of the juices extracted from over fifty fruits, leaves, stems, etc., of plants. In the case of fruits the pressures varied from 5·94 atm. for a specimen of *Lycopersicum esculentum* to 28·27 to 29·53 atm. for *Prunus communis*, the high numbers in the latter case being due probably to the sugars. *Citrus Limonum* gives larger variations, 10·46 to 12·21 atm. for samples obtained in August, and 12·05 to 14·06 atm. for those obtained in February. The pressure in the rind is somewhat lower. The red stems of *Rheum officinale* gave 6·52 atm., this low number being associated with the relatively low molecular weight of oxalic acid, the chief constituent of the juice.

The pressure in the underground organs studied ranged from 6·5 atm. in the tubers of *Solanum tuberosum* to 18·7 atm. in the tubers of *Helianthus tuberosus*.

Calculations of the mean molecular weight showed that the red stem of *Rheum officinale* gave the lowest value, 76, and the tubers of *Helianthus tuberosus* the highest value, 394. The fruits gave values varying from 110 to 231.

The author concludes that similar plant organs of the same species have approximately equal osmotic pressures, but this deduction does not apply to leaves.

E. J. R.

Hydrocarbons of Vegetable Origin. TIMOTHÉE KLOBB, JULES GARNIER, and R. EHRWEIN (*Bull. Soc. chim.*, 1910, [iv], **7**, 940—950. Compare Klobb and Fandre, Abstr., 1907, ii, 123).—Methods for the isolation of hydrocarbons occurring in plants are described, and a number of the hydrocarbons are characterised. Many similar saturated hydrocarbons of vegetable origin have been described by Power and his collaborators.

The plant material, usually flowers, is extracted with either cold or warm light petroleum, and the soft extract left on removal of most of the solvent is dissolved as far as possible in boiling acetone. From the filtered hot acetone solution the hydrocarbon separates on cooling, and may be purified if necessary by boiling with potassium hydroxide

in alcohol and subsequent recrystallisation from ether or acetone. An alternative process consists in treating a concentrated alcoholic extract of the flowers with aqueous ammonia solution (15—20%) for several days to remove tannins, etc., and then extracting with ether. The residue left on distilling off the ether is treated with potassium hydroxide in alcohol, the solvent distilled off, and the residue poured into water and extracted with ether. The residue from the last solvent is extracted with boiling alcohol, which, on cooling, deposits the hydrocarbon in crystalline form. These hydrocarbons dissolve in warm light petroleum, chloroform, or carbon disulphide, and can be obtained in microscopic crystals from boiling acetone or alcohol, but they assume a more definitely crystalline form if left in contact with acetone during one or two days, or if obtained by slow evaporation from dilute solutions in ether. The melting point varies from 53° to 65° (Maquenne block). They are unaffected by bromine or potassium permanganate.

The flowers of *Arnica montana* yield, in addition to arnidiol (Abstr., 1904, i, 410; 1905, i, 594), a mixture of hydrocarbons, from which *one* having the formula $C_{30}H_{62}$, m. p. 62°, has been isolated in a pure state (compare Börner, *Inaug. Diss.*, Erlangen, 1892). *Matricaria chamomilla* flowers, treated by the second general process, furnish a *hydrocarbon*, $C_{29}H_{60}$, m. p. 52—54°, which crystallises in colourless lamellæ. The *hydrocarbon*, $C_{28}H_{58}$, from *Antennaria dioica*, m. p. 64—66°, crystallises in nacreous lamellæ from acetone. Worm seeds (flowers of *Artemisia maritima*) yield a *hydrocarbon*, $C_{32}H_{66}$, m. p. 55—58°, which crystallises in colourless lamellæ, and even after purification evolves hydrogen bromide with bromine in carbon tetrachloride. The *hydrocarbon*, $C_{27}H_{56}$, from *Tussilago farfara* flowers, m. p. 57—59°, forms nacreous, hexagonal lamellæ. The flowers of *Tilia europea* yield a *hydrocarbon*, $C_{28}H_{58}$, m. p. 54—56°. The hydrocarbon isolated by Naudin from chamomile flowers (Abstr., 1884, 391) is shown to have the formula $C_{30}H_{62}$; it melts at 64°, and crystallises slowly from ether in colourless lamellæ.

The formulæ assigned to the various hydrocarbons have been controlled in most cases by cryoscopic determinations in naphthalene.

T. A. H.

Formation and Distribution of Certain Alkaloids in Papaver somniferum. M. KERBOSCH (*Pharm. Weekblad*, 1910, **47**, 1062—1074, 1081—1094, 1106—1119).—An investigation of the formation and distribution of the alkaloids of *Papaver somniferum* in the different parts of the plant at various stages of its growth. The seed contains a trace of narcotine and amorphous alkaloids. After three days' germination, the seeds have developed an appreciable quantity of narcotine, and the alkaloids make their appearance in the plant in the order: narcotine, codeine, morphine, papaverine, narceine, and thebaine. When the plants are 5—7 cm. high they contain the four alkaloids first named, and they are present in all the organs of the plant from the time of flowering until it reaches maturity, when all the organs contain narcotine, codeine, and morphine. The composition of the sap differs in different parts of the plant. Germina-

tion of the seeds in an atmosphere free from nitrogen also produces narcotine, its formation being occasioned by the decomposition of proteins. The proportion of narcotine in the buds is much greater than in the unripe seed husks.

With a solution of cadmium iodide (1·8 gram) and cæsium iodide (5 gram) in 100 c.c. of water, papaverine, codeine and morphine yield additive products readily identified by their crystalline form. On addition of the reagent, each of the six alkaloids gives an amorphous precipitate; on warming, the additive products of those named dissolve, and crystallise on cooling, whilst those of the others remain amorphous. A. J. W.

Chemical Examination of the Bark of a Species of Prunus. HORACE FINNEMORE (*Pharm. Journ.*, 1910, [iv], 31, 604—607).—A spurious substitute for *Prunus serotina* bark, which is very similar to the bark of *P. emarginata,* has been examined and found to differ from the true bark in containing no cyanogenetic glucoside yielding benzaldehyde on hydrolysis (Power and Moore, Trans., 1909, **95**, 243). It contains quercimeritrin (Perkin, Trans., 1909, **95**, 2181), a new colouring matter glucoside (prunitrin), and a phytosterol as its principal constituents.

A concentrated alcoholic extract of the bark was dissolved in water and extracted with ether, which caused the precipitation of some impure prunetin (see below), but dissolved a mixture of (1) an *acid substance*, m. p. 121°, crystallising in plates, and giving a reddish-purple coloration with ferric chloride solution; (2) a *phytosterol*, m. p. 137°, which furnished an *acetyl* derivative, $C_{27}H_{45}OAc$, m. p. 121°, crystallising in lustrous plates; (3) fatty matter furnishing the same phytosterol and formic, butyric, and palmitic acids on hydrolysis; (4) *prunetin*, $C_{16}H_{12}O_5$, m. p. 242° (corr.), which crystallises in colourless needles, dissolves in alkalis with a yellow colour, but is sparingly soluble in organic solvents. It furnishes a *monoacetyl* derivative, m. p. 190°, a *diacetyl* derivative, m. p. 224—226° (corr.), and a *dibenzoyl* derivative, m. p. 215°, all of which crystallise well. On treatment with methyl iodide and sodium methoxide it yields a *monomethyl ether*, m. p. 145°, crystallising in flat, lustrous needles, and this in turn gives a *monoacetyl* derivative, m. p. 202°, crystallising in colourless prisms. When heated with hydriodic acid, prunetin furnishes 1 mol. of methyl iodide, and *prunetol*,

$$C_{15}H_{10}O_5,$$

m. p. 290°, which crystallises in colourless needles, yields a *triacetyl* derivative, m. p. 205°, and on methylation furnishes a mixture of prunetin methyl ether (see above), and a second *product*, which is insoluble in ether and furnishes a crystalline *acetyl* derivative, m. p. 186°. Both prunetin and prunetol, on solution in boiling acetic acid and addition of sulphuric acid, furnish unstable *sulphates* of the type described by Perkin and Pate (Trans., 1895, **67**, 644). On fusion with potassium hydroxide, prunetin yields *p*-hydroxyphenylacetic acid and a substance which gives the reactions of phloroglucinol, and furnishes methyl iodide on treatment with hydriodic acid. It is considered that

prunetin is closely related to scutellarein (Molisch and Goldschmiedt, Abstr., 1902, i, 48) in constitution, and may have the formula

$$\begin{array}{l} \mathrm{OMe{\cdot}C{-\!-}CH{=\!=}C{-}O{-}CH\quad CH{=}CH{-}C{\cdot}OH} \\ \mathrm{\quad\quad\ CH{\cdot}C(OH){=}C{-}CO{-}C{-\!-}C{=\!=}CH{-}CH} \end{array} .$$

The aqueous solution, after extraction with ether, deposited on standing crystals of quercimeritrin (Perkin, Trans., 1909, **95**, 2181).

The aqueous extract on defaecation with lead acetate and subsequent extraction with ethyl acetate furnished a new glucoside, *prunitrin*, $C_{22}H_{24}O_{11}$, crystallising from hot water in slender needles. This, on hydrolysis with hydrochloric acid, yielded prunetin and dextrose, and is probably the source of prunetin in the bark. Yellow colouring matters also occur in *Prunus cerasus* and *P. avium* barks.

T. A. H.

The Resistibility of Wheat and Barley to Poisons and its Importance for Sterilisation. HEINRICH SCHROEDER (*Centr. Bakt. Par.*, 1910, ii, **28**, 492—505).—The following method was found to be suitable for sterilising wheat and barley grains. The seeds are first well washed in running water, and then immersed in 5% silver nitrate solution for eighteen to twenty-four hours. They are then washed with water, and allowed to swell in a dilute solution of sodium chloride.

The method would presumably be suitable for other seeds, such as rice and oats, which are protected similarly to wheat, but it does not seem suitable for sterilising leguminous seeds.

Only undamaged seeds can be sterilised with silver nitrate.

N. H. J. M.

Influence of Some Artificial Oxydases and of Some Metallic Compounds on the Growth of Wheat. V. NASARI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 361—367).—From experiments on the germination of wheat in the laboratory and also its growth under agricultural conditions, the authors find that compounds of manganese (dioxide, sulphate, carbonate) exert a favourable influence on the result obtained. The manganese compounds were supplied to the plant in three ways: (1) as a component of an artificial oxydase, with which the seeds were enveloped; (2) as a component of a paste containing starch and nitrogenous organic matter, with which the seeds were covered; (3) as a fertiliser. Ferric oxide may also have a beneficial effect, but ferrous sulphate only prevents mildew. Copper and aluminium sulphates affected growth unfavourably. R. V. S.

Putrefaction Bases from the Decomposition of Soy Beans (Glycine hispida). KIYOHISA YOSHIMURA (*Biochem. Zeitsch.*, 1910, **28**, 16—22. Compare Abstr., 1909, ii, 928).—The following bases can be isolated from the products formed when soy beans are boiled with water, the moist beans rubbed in a mortar until the whole has a pasty consistency, and left for some four months at the ordinary temperature: β-amino-4-ethylglyoxaline (β-iminoazolylethylamine: Ackermann, this vol., i, 419), 0·18; tetramethylenediamine, 0·25;

pentamethylenediamine, 0·53; trimethylamine, 0·23; ammonia, 4·60. The numbers refer to grams per kilo. of air-dried material.

Histidine, arginine, and lycine could not be detected. J. J. S.

Harmlessness of Sulphurous Acid in Wines. P. CARLES (*Ann. Chim. anal.*, 1910, **15**, 419—421; *Bull. Soc. chim.*, 1910, [iv], **7**, 998—1001).—The author emphasises the non-injurious effects of sulphurous acid, points out the necessity of using this acid in the manufacture of certain classes of wines, and draws attention to a report recently issued (this vol., ii, 734) which deals with this subject.
W. P. S.

Importance of Osmotic Pressure and of Electrolytic Conductivity in Judging Soils. JOSEF KÖNIG, JULIUS HASENBÄUMER, and H. MEYERING (*Landw. Versuchs-Stat.*, 1910, **74**, 1—56).—The estimation of the osmotic power of taking up water yields good results when a constant temperature (18—20°) is maintained. The process can also be employed for the estimation of the mol.-wt. of substances not, or only slightly, subject to diosmosis.

Estimation of electrolytic conductivity of soils generally yields values closely related to the osmotic power of taking up water. Both are considerably increased by the usual manures, and diminished by the growth of plants, so that both give expression to the degree of solubility of plant nutrients in the soil. Electrolytic conductivity is more readily estimated than the osmotic taking up of water; the latter seems, however, to furnish the more trustworthy results.

As electrolytic conductivity increases as the size of soil particles diminishes, a constant degree of fineness, not exceeding 1 mm., should be employed.

The potassium and phosphoric acid of dipotassium phosphate are completely absorbed up to a certain point; sulphates are partly absorbed, whilst nitrates and chlorides are not absorbed at all.

Increased yields are obtained by treating exhausted soils containing complex humates or humus colloids with hydrogen peroxide.

Growth of clover resulted in increased amounts of soluble nutrients in the soil. N. H. J. M.

The Ammonia in Soils. EDWARD J. RUSSELL (*J. Agric. Sci.*, 1910, **3**, 233—245).—Soil contains a number of nitrogenous compounds that readily evolve ammonia on treatment with alkalis. In order to discriminate between these and the true ammonium compounds present, the author investigated the relationship between the concentration of alkali and evolution of ammonia when soil was distilled with alkalis under diminished pressure. The resulting curves show that two stages exist; in the first, the ammonium compounds are decomposed; in the second, other nitrogen compounds break down. The two stages are very marked when either magnesium oxide or alcoholic potash is used as the alkali, and therefore the author uses either of these in determining the ammonia free or combined in soils.

A number of determinations show that ammonia is present only in minute amounts in normal soils, although when nitrification was

stopped, marked accumulations occurred. It follows that the rate of nitrification must be greater than that of ammonia production, and in normal conditions is limited by this rate. In the light of this observation, it is shown that the various methods in vogue for studying the rate of nitrification in soil really deal with three separate things: the rate of ammonia production in soils, the rate of nitrate production in soils, and the rate of nitrification in a culture solution; the discordance of the results is therefore explained.

When ammonium salts are added to soil a certain proportion enters into a stable combination that is not decomposed on distillation with alcoholic potash or magnesia, and is therefore not an ammonium compound. Its constitution, however, has not been determined.

E. J. R.

Biochemical Resolution of Phosphoric Acid in Soils. RENATO PEROTTI (*Bied. Zentr.*, 1910, **39**, 717—718; from *Staz. sper. agrar. ital.*, 1909, **42**, 537—538).—The solution of phosphoric acid in ordinary soils depends on the action of acids producing bacteria, and is increased by the presence of carbohydrates, especially disaccharides, and of ammonium sulphate. Ammonium tartrate is indifferent, whilst ammonium nitrate gives sometimes positive and sometimes negative results. Calcium and magnesium carbonates retard the action of the bacteria, whilst alumina is more indifferent, and ferric oxide is somewhat favourable. N. H. J. M.

Suitability of the Calcium of Calcium Silicate for the Nutrition of Plants. HANS MIETH (*Landw. Versuchs-Stat.*, 1910, **74**, 81—120).—Calcium in the form of silicates is readily utilised by plants, and far more silica is taken up than calcium. The silicates are decomposed by plants with production of free silicic acid and calcium carbonate.

In estimating the available calcium in soils, it is necessary to include silicates as well as carbonate. N. H. J. M.

Analytical Chemistry.

New Normal Solution and Reagent Bottle. FRANK M. DAVIS (*J. Amer. Chem. Soc.*, 1910, **32**, 1277—1279).—The normal solution bottle described consists of a long, narrow bottle provided with a ground glass cap, furnished with a groove to admit air when desired. The bottle has two side-tubes, one near the top, and the other near the bottom. To these is fused a wider tube, graduated like a burette, and having a delivery tube at the lower end. This delivery tube is provided with a glass stopcock, and another stopcock is placed in the lower of the two tubes connecting the burette with the bottle.

The apparatus is supported in a light wooden frame suspended by trunnions between two triangular racks.

On opening the stopcock between the burette and bottle, adjusting the cap of the bottle so that air can enter, and tilting the apparatus forward if needful, the solution flows from the bottle into the burette. The stopcock is then closed, and the bottle replaced in an upright position. The liquid can now be drawn off from the burette as required.

The reagent bottle is of similar construction, but the burette is set into the wall of the bottle, so that the apparatus can be held in the hand, and a support is not necessary.

The advantages of these forms of apparatus are that measured quantities of the reagent can be withdrawn from the bottle without recourse to measuring cylinders or pipettes, and that the risk of extraneous matter being admitted into the reagent is obviated.

E. G.

A Very Sensitive Indicator. JULIUS F. SACHER (*Chem. Zeit.*, 1910, **34**, 1192).—Radish skins are extracted for a few hours with their own weight of 96% alcohol, and should the liquid show any acidity to litmus paper, it is carefully neutralised with *N*/100-potassium hydroxide. This solution, 2 c.c. of which are added to 50 c.c. of the liquid to be tested, makes an excellent indicator for both acid and alkalis, turning intensely red with the former, and green with the latter. It is more delicate than methyl-orange or phenolphthalein, but, like the latter, it is affected by carbon dioxide. L. DE K.

Rupp and Loose's Indicator. IWAN I. VON OSTROMISSLENSKY and I. S. BABADSCHAN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 609—611. Compare Abstr., 1908, ii, 90).—Rupp and Loose's methyl-red is a very delicate indicator for alkali hydroxides, but the authors were unable to isolate it by the method described by Rupp and Loose. By employing the theoretical quantity of dimethylaniline, extracting the products of reaction with ether or chloroform, and evaporating the latter, the substance was isolated, but it could not be purified by recrystallisation. Z. K.

A Delicate Reaction for Hydrogen. CONSTANTIN ZENGELIS (*Zeitsch. anal. Chem.*, 1910, **49**, 729—732).—The process is based on the fact that platinum and palladium absorb hydrogen, and then exercise a reducing action when heated with molybdenum solution. This is made by dissolving 1 gram of molybdenum trioxide in dilute sodium hydroxide, acidifying the liquid with hydrochloric acid, and diluting to 200 c.c.

The gas to be tested is first passed through a wash-bottle containing aqueous sodium hydroxide. The end of the delivery tube dipping into a test-tube containing a few c.c. of the reagent is tied over with platinum gauze, and if hydrogen is present in not too minute a quantity, the solution will turn blue.

A still more delicate test is to allow the gas to come in contact with spongy palladium heated at 80—120° in an atmosphere of carbon dioxide. A convenient apparatus is described for this purpose. The

palladium is then warmed with molybdenum solution to see if there is any reduction. L. DE K.

Electrolytic Estimation of Chlorine in Hydrochloric Acid with the Use of a Silver Anode and a Mercury Cathode. JACOB S. GOLDBAUM and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, **32**, 1468—1471).—As a result of criticism of the electrolytic method (Abstr., 1907, ii, 574, 988; 1908, ii, 1072) for the estimation of chlorine when applied to solutions containing free hydrochloric acid, the authors have made further experiments. It is shown that satisfactory results can be obtained if certain precautions are taken. Silver is deposited on the platinum gauze anode by electrolysis of a cyanide solution, and the electrode is then dipped in dilute hydrochloric acid, washed thoroughly with distilled water, and ignited to incipient redness in a Bunsen flame. By this means any admixed cyanide is completely removed.

To obviate the disturbing effect of the formation of oxide on the anode, the latter is placed for ten to fifteen minutes in an electric oven heated to 300°, when the silver oxide is completely decomposed.

Experimental data are recorded which show that the estimation of chlorine in hydrochloric acid can be effected without appreciable error if the above precautions are observed. Similar data are given for the electrolytic estimation of bromine and hydrobromic acid, but the results appear to be rather low. H. M. D.

Catalytic Action of Silver Salts [on Chlorates in Presence of Aniline Hydrochloride]. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1910, **8**, 222—226).—Traces of silver very much intensify the colour produced by the action of a chlorate on the solution of aniline hydrochloride employed in the author's method of estimating chlorates colorimetrically (Abstr., 1909, ii, 179). It is therefore necessary if silver nitrate has been used as a means of removing other substances present (for example, ferricyanides) to ensure that any excess of silver is eliminated by the addition of sodium chloride before proceeding to estimate chlorates. The manner in which the silver acts is uncertain, but possibly it exerts a catalytic action, by which the velocity of the change producing the coloration is accelerated. The sensitiveness of the method formerly described can be much increased by adding one or two drops of a 1% solution of silver nitrate before adding the aniline reagent; in presence of silver, traces of chlorate, which ordinarily cannot be detected or estimated, give a distinct coloration. Thus 2 grams of sodium nitrate containing 0·00005 gram of chlorate usually gives a coloration only after several minutes; in presence of silver, 0·2 gram of the nitrate produces far more coloration after a few seconds. This simplifies the examination of refined nitres containing less than 0·0001 gram of chlorate.

Traces of copper and of chloroplatinic acid excerise a similar action to silver in increasing the colour, but, unlike silver, they appear to retard its production. W. A. D.

Weszelszky's Method for Estimating Bromine and Iodine. JOSÉ CASARES GIL (*Anal. Fis. Quim.*, 1910, **8**, 33—40).—Tests made

of the accuracy of Weszelszky's method (Abstr., 1900, ii, 436) for estimating the amount of iodine in known weights of dissolved iodide showed that heavy loss of iodine occurs if attempts are made to remove by direct evaporation the excess of chlorine used in oxidising the iodide to iodate. If, however, the excess of chlorine is eliminated by aspirating a rapid current of air through the hot acid solution, accurate results are obtained.

Contrary to Weszelszky's statement, potassium chlorate liberates traces of iodine from potassium iodine in presence of hydrochloric acid under the conditions used in the method; on adding 0·029 gram of potassium chlorate dissolved in 125 c.c. of distilled water to 5 c.c. of 10% potassium iodide and 5 c.c. of hydrochloric acid, 3 drops of $N/10$-sodium thiosulphate are required to destroy the iodine, using starch as indicator in the usual way. If the chlorate is dissolved in only 15 c.c. of water, 5 drops of $N/10$-thiosulphate are required. To convert the sodium hypochlorite formed during the oxidation of bromides in Weszelszky's method by chlorine in alkaline solution entirely into chlorate, it is absolutely necessary to evaporate to dryness and heat the residue for some time on the water-bath. Control analyses made with pure potassium bromide show that Weszelszky's method gives fairly accurate results. W. A. D.

Precipitation of Sulphate Ions as Barium Sulphate. ERNST RUPPIN (*Chem. Zeit.*, 1910, **34**, 1201).—The following method is recommended. The solution (250 c.c., furnishing about 1·5 grams of barium sulphate) is slightly acidified with hydrochloric acid and heated to boiling. Boiling solution of barium chloride (200 grams per litre) is then added all at once in excess of about 50%, and the whole set aside until the following day. The mother liquor is decanted through a filter, and the precipitate digested with 125 c.c. of very dilute nitric acid during fifteen minutes, the clear liquid being decanted through the same filter, and the filtrate and washings collected and concentrated to 200 c.c. To this, 2 c.c. of saturated barium nitrate solution are added, and after thirty minutes the precipitate is filtered off and washed. The main precipitate is then collected on a filter and dried at 100°. The two filter papers are burnt and their ash added to the precipitate, and the whole ignited and weighed with the usual precautions.

A less accurate, but quicker, method consists in precipitating the sulphate by the use of a 20% solution of barium chloride in an excess of about 33%, filtering after about thirty minutes, washing the precipitate with about 100 c.c. of boiling water by decantation, and continuing the washing on the filter paper until the wash-water is free from chlorides. T. A. H.

Estimation of Organic Matters in Spent Sulphuric Acids. RUD. MICHEL (*Chem. Zeit.*, 1910, **34**, 1210—1211).—The apparatus consists of a round-bottomed flask fitted with a stopcock funnel, and connected by means of a bent capillary tube to the three-way tap of an ordinary gas burette filled with water. Into the flask are introduced 20 c.c. of a saturated solution of potassium permanganate, and into

the funnel is placed a known volume of the acid to be tested. The tap at the lower end of the burette being opened, the acid is admitted slowly into the flask, when carbon dioxide is evolved and enters the burette. The remaining gas is expelled from the flask by introducing water through the funnel until the liquid reaches the three-way tap. The burette is now closed, and the volume of gas read off with the usual precautions. The exact volume of carbon dioxide is then found by absorption with aqueous potassium hydroxide in the usual manner.

The carbon dioxide is calculated to its weight of carbon ; 75 parts of the latter average 100 parts of (resinous) organic matter.

L. DE K.

Use of Nitron in the Analysis of Nitrates. ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 567—570. Compare Gutbier, Abstr., 1905, ii, 418).—A somewhat modified form of Busch's gravimetric estimation of nitric acid in nitrates by means of nitron.

The weighed substance is dissolved in 100 c.c. of water and boiled, after which 10—12 drops of dilute sulphuric acid are added for every 0·1 gram of NO_3, and 10 c.c. of a 10% solution of nitron in 5% acetic acid. After cooling, the beaker is surrounded by ice for five to eight hours, at the end of which time the solution is filtered through a Gooch crucible containing Swedish filter paper instead of asbestos. The precipitate is washed five to seven times with 3—6 c.c. of a saturated solution of nitron nitrate cooled to 0°, and finally once with 3—5 c.c. of water at 0°. It was then dried at 105—110°. The method gives good results, and is evidently independent of the nature of the metal.

Z. K.

Detection and Estimation of Arsenic Acid in Presence of Arsenious Acid by means of Magnesia Mixture. JOHANNES C. BRÜNNICH and F. SMITH (*Zeitsch. anorg. Chem.*, 1910, **68**, 292—296). —The experiments of Lutz and Swinne (Abstr., 1909, ii, 1052) have been repeated, using weaker arsenite solutions, such as are employed for agricultural analyses. The best results are obtained by using a magnesia mixture containing 5·5% magnesium chloride, 10·5% ammonium chloride, and only 1·4% ammonia. With such a solution a distinct crystalline precipitate is obtained in ten minutes from a solution containing only 0·0002 gram As_2O_5, alone or in the presence of 0·025 gram As_2O_3. The addition of ammonia, although generally recommended, is disadvantageous.

The separation is quantitative if the quantity of arsenite present does not much exceed 0·5% As_2O_3. The quantity of alkali salts present should not exceed an original content corresponding with 1% NaOH. Citrates completely prevent the precipitation of arsenates.

C. H. D.

Apparatus for the Estimation of Carbon, Arsenic, and Sulphur in Iron and Steel. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1910, **23**, 1980—1981).—The apparatus is essentially the same as that described and figured previously (this vol., ii, 893). It consists of

a flask for dissolving the material, furnished with a specially constructed side-tube, through which the acid is introduced and through which may be also passed a current of carbon dioxide, or of purified air, to sweep out the last remnants of hydrogen sulphide or carbon dioxide, as the case may be. In the neck of the flask is ground a condensing apparatus, which, in the case of sulphur or arsenic estimations, is connected to a pipette-like delivery tube, which plunges to the bottom of a beaker containing the absorbent. If strong hydrochloric acid is employed, as in sulphur estimations, the gases should be washed before entering the body of the pipette, and for this purpose the latter is furnished inside at its upper end with a glass bulb having a small hole to allow the gases to escape; the bulb is half filled with water. A more simple form of apparatus, in which the side-tube is absent, is also described; the hydrogen sulphide is then finally expelled by using a solution of sodium hydrogen carbonate, and allowing this to run into the acid liquid. L. DE K.

Estimation of Carbon and Sulphur in High-percentage Alloys of Tungsten, Molybdenum, and Vanadium with Iron. ERICH MÜLLER and BERNARDO DIETHELM (*Zeitsch. angew. Chem.*, 1910, **23**, 2114—2124).—Comparison estimations by different methods of carbon in high-percentage alloys of tungsten, molybdenum and vanadium with iron show that the only trustworthy method is the dry combustion with oxygen. This method, besides giving trustworthy results, has the advantage that the sulphur can be determined at the same time.

The combustion is carried out in a porcelain tube, glazed externally, which is 800 mm. long, and has an internal diameter of 20 mm. The part containing the alloy is enclosed in a Heraeus electric resistance furnace, 420 mm. long, and heated to 1100°. Part (189 mm.) of the remainder of the tube is enclosed in a drying oven, and heated to 350°; this part contains lead peroxide, which has been treated according to Dennstedt's method, and is used for absorbing the oxides of sulphur. Succeeding the porcelain tube is a combustion tube (300 mm.), half filled with lead chromate, and half with copper oxide; this is heated in an ordinary furnace, and serves the purpose of oxidising any carbon monoxide to dioxide. The carbon dioxide is absorbed in soda-lime, first passing through concentrated sulphuric acid to dry it. The sulphur absorbed by the lead peroxide is determined by Dennstedt's method.

The alloy used should be in the form of pieces 2—3 mm. in diameter. For the determination of carbon in the ordinary kinds of iron, the method described has no advantages over the ordinary wet combustion with chrom-sulphuric acid. T. S. P.

A Method for Purifying and Drying Organic Liquids by Wiping. C. LORING JACKSON and AUGUSTUS H. FISKE (*Amer. Chem. J.*, 1910, **44**, 5, 438—441).—A method is described for drying organic liquids prior to analysis by wiping with strips of moist filter paper. Experiments with chlorform show that the error due to the residual moisture is slight. N. C.

[Analysis of Gases from Mineral Springs.] F. Henrich (*Zeitsch. angew. Chem.*, 1910. **23**, 1809, 2358—2359); Ernst Hintz and Leo Grünhut (*ibid.*, 1910, **23**, 2125—2126, 2359).—Polemical (compare this vol., ii, 356). T. S. P.

Estimation of the Alkali Carbonates and of the Metals of the Alkaline Earths in Potable and Mineral Waters. Ezio Comanducci (*Boll. chim. farm.*, 1910, **49**, 714—716).—The estimation of the alkalinity of a water by boiling it gives results which are always too high, because the solubility of the carbonates of calcium and magnesium depends on the composition of the water and the duration of the boiling. The ebullition must be conducted in a platinum vessel, for the author's experiments show that even Jena glass gives up some alkali when boiled with ordinary water, or with distilled water containing calcium and magnesium hydrogen carbonates, although it is not acted on by distilled water. The determination of calcium and magnesium salts soluble after boiling also gives somewhat high results. R. V. S.

Estimation of the Alkalis; Removal of the Ammonium Salts. Josef Jámbor (*Zeitsch. anal. Chem.*, 1910, **49**, 733—734).—The solution obtained in the usual manner is evaporated on the water-bath until a crust of ammonium salts begins to form. The dish is then removed from the water-bath, and half the volume of sulphuric acid is added. The whole is now heated over a small flame until the free acid and the ammonium sulphate have been completely expelled; the operation does not require constant attention. L. de K.

Colour Test for Salts of Zinc. II. Angel del Campo y Cerdán (*Anal. Fis. Quim.*, 1910, **8**, 279—281).—In the method formerly described (Abstr., 1909, ii, 439) a fixed alkali cannot be used in place of ammonia. On the other hand, the ethereal solution of resorcinol can often be replaced with advantage by an alcoholic aqueous solution of resorcinol, as the velocity of the change is thereby increased, especially on warming. With an aqueous solution, the colour appears instantly on boiling.

Nickel salts give with the resorcinol test a similar coloration to zinc, but less blue. With cobalt salts the reagent accelerates the formation of the red colour of the cobaltammines. Manganese interferes with the test for zinc. Chromium, unless present in large quantity, does not interfere. Aluminium and iron do not interfere, as the test is carried out in ammoniacal solution.

Copper and cadmium interfere with the test, and must be previously eliminated. Oxidising and reducing agents also make it worthless. W. A. D.

Use of Organic Electrolytes in Cadmium Separations. Mary E. Holmes and Mary V. Dover (*J. Amer. Chem. Soc.*, 1910, **32**, 1251—1256).—In an earlier paper (Holmes, Abstr., 1909, ii, 184) it was shown that cadmium can be separated from certain other metals by the use of low currents when the rotating anode is

employed. Further work on this subject has now been carried out. The alkaline-earth metals were used, and the acetate, formate, and lactate electrolytes described by Davison (Abstr., 1905, ii, 859). Corresponding separations were made with low currents (0·3 ampere) and with high currents (5 amperes).

The results show that low currents are preferable for the deposition of cadmium when organic electrolytes are used. It was observed that each electrolyte exerts a marked influence on the character of the deposit. The best deposits were obtained in presence of a mixture of ions, and especially in presence of the sulphate ion. The formate ion exercises a good influence on the character of the deposit, cadmium acetate solution with the formate electrolyte, and cadmium formate solution with the lactate electrolyte, giving satisfactory results, even in presence of the alkaline-earth metals. The acetate and lactate electrolytes when used alone were not so successful.

E. G.

Colorimetric Estimation of Lead in Potable Water. K. SCHERINGA (*Pharm. Weekblad*, 1910, **47**, 1212—1213. Compare Egeling, Abstr., 1907, ii, 398).—From the results of experiments, the author concludes that Egeling's colorimetric method for the estimation of lead in potable water is untrustworthy.

A. J. W.

Electrolytic Separations. IRVING H. BUCKMINSTER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1910, **32**, 1471—1477).—The results of a large number of experiments relating to the separation of pairs of metals by electrolysis are communicated. The conditions under which the following separations were effected are briefly described: Mercury and bismuth from nickel in presence of sulphuric acid; copper, mercury, and lead from nickel in presence of nitric acid; zinc from nickel in an alkaline tartrate solution; copper from nickel in presence of free phosphoric acid. Silver also can be separated from nickel in presence of free nitric acid if a little alcohol is added to the solution. In the separation of nickel from aluminium in an ammoniacal ammonium sulphate solution, the deposited nickel is contaminated with aluminium hydroxide; if, however, a little sodium hydroxide is added, the hydroxide is dissolved, and good results are obtained. Nickel can also be separated from magnesium, and the alkaline-earth metals in an ammoniacal ammonium salt solution. From this solution nickel is not deposited if chromium or cobalt salts are present, and it has been found that cobalt-ammonia compounds are formed in the latter case.

Other experiments have reference to the deposition of zinc from a cyanide solution, the separation of silver and mercury from bismuth in nitric acid solution, of uranium from zinc, and of cobalt and nickel from uranium.

H. M. D.

Conditions Affecting the Electrolytic Estimation of Copper. WALTER C. BLASDALE and W. CRUESS (*J. Amer. Chem. Soc.*, 1910, **32**, 1264—1277).—The difficulties encountered in the application of the

electrolytic method to the analysis of pyritiferous ores are enumerated, and means are indicated for overcoming them.

When 1 gram samples of such ores are used, the resulting solution may possibly contain 0·2 gram of copper, 0·4 gram of iron, and variable quantities of zinc, arsenic, and lead. If arsenic is absent, the copper can be completely separated within ninety minutes by the use of the Winkler electrode and a current of 0·75 ampere, provided that the volume does not exceed 100 c.c. and the solution does not contain any nitric acid or more than 5 c.c. of concentrated sulphuric acid. If arsenic is present, the solution should be electrolysed under the conditions already specified, and the deposit dissolved in nitric acid and again electrolysed; or, if the amount of arsenic is small, good results can be obtained by a single precipitation if 1—2 c.c. of nitric acid and 5 grams of carbamide are added to the solution. E. G.

Collection of Colloidal Precipitates. MORTON LIEBSCHUTZ (*Chem. News*, 1910, 102, 213).—In the analysis of bronzes, the tendency of metastannic acid to pass through the filter may be overcome by heating it with a dilute solution of albumin, which coagulates the colloidal precipitate. The latter has afterwards to be boiled with dilute nitric acid to remove adsorbed copper.

In separating zinc and copper by the cyanide method, the copper cyanide is removed by decantation, and to the solution containing the zinc sulphide in suspension, a little lead acetate is added. The zinc and lead sulphides can then readily be collected; the former is dissolved by boiling with dilute hydrochloric acid, and titrated with potassium ferrocyanide. G. S.

Estimation of "Carborundum" in Fragments of Coke Crucibles. HENRYK WDOWISZEWSKI (*Chem. Zeit.*, 1910, **34**, 1209—1210).—One gram of the finely-powdered material is ignited to burn the coke, and the weighed residue is analysed as usual for silica and bases. If carborundum is present, it is obvious that the sum total of the various constituents must exceed 100%; by multiplying the excess by two, the amount of carborundum is obtained.

The accuracy of the result, of course, depends on the care bestowed on the analytical operations. L. DE K.

Assay of Aluminium Ores. JUAN CALAFAT Y LEÓN (*Anal. Fis. Quim.*, 1910, **8**, 281—286).—To ascertain whether a mineral is suitable as a source of aluminium, roughly 0·5 gram of the finely-powdered substance is intimately mixed with an equal volume of powdered anhydrous sodium carbonate and heated on charcoal in an oxidising flame during several minutes. The product is extracted with water, the solution filtered, and carbon dioxide passed through the filtrate. If the ore is of any value as a source of aluminium, the carbon dioxide will precipitate aluminium hydroxide from the solution of aluminate. The method can be made roughly quantitative by comparing the height of the precipitate obtained after settling in a tube of fixed diameter with that obtained from 0·5 gram of bauxite under similar conditions. The method is very rapid, and is useful when a large number of

minerals have to be examined to ascertain their fitness as ores of aluminium. Ordinary clay, kaolin, and other forms of aluminium silicate do not indicate the presence of alumina in this test.

W. A. D.

Detection and Estimation of Manganese in Wine. DUMITRESCOU and (Mlle.) E. NICOLAU (*Ann. Falsif.*, 1910, **3**, 407—410).—When the ash of a wine containing manganese is heated with ammonium persulphate solution in the presence of a trace of cobalt nitrate, the pink permanganate coloration obtained is not proportional to the amount of manganese present, as the latter is partly precipitated as its hydroxide. It is therefore recommended that the heating be prolonged for thirty minutes, and that the cobalt nitrate be omitted when it is desired to estimate the quantity of manganese present. Under these conditions the whole of the manganese is precipitated, and may be collected and weighed. The authors have estimated the quantity of manganese in 52 samples of various white and red wines, the quantities found varying from 1·8 to 27 mg. per litre.

W. P. S.

Electrolytic Separation of Nickel and Cobalt. PIERRE BRUYLANTS (*Bull. Soc. chim. Belg.*, 1910, **24**, 367—372).—The description given by Piñerûa Alvarez of his method for the electrolytic separation of nickel and cobalt is not detailed enough, and the author has not been able to obtain satisfactory results. Both the metal deposited and the solution remaining after electrolysis contained nickel and cobalt, and the results are not even approximately accurate.

The following method is suggested: To a solution containing the sulphates of nickel and cobalt is added potassium cyanide until the precipitate first formed just redissolves. The solution is then oxidised with bromine water and acid added. The nickel ions thus produced form nickel cobalticyanide, which is insoluble in acids, but soluble in ammonium hydroxide, giving a solution containing the ions $Ni(NH_3)_6^{\cdot\cdot}$ and $Co(CN)_6'''$. Electrolysis of the resulting solution, using Sand's apparatus and a graded potential, leads to the deposition of nickel, but in all the experiments so far carried out the nickel has contained 2—4% of cobalt.

T. S. P.

Estimation of the Amount of Molybdenum in Calcium Molybdate. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1910, **23**, 1981).—0·5 Gram of the finely-powdered compound is boiled with 20 c.c. of strong hydrochloric acid and 1—2 c.c. of strong nitric acid. The solution is diluted to 150 c.c., and, without filtering, poured into an excess of ammonia, to which a few c.c. of yellow ammonium sulphide have been added. After heating for a few minutes on the water-bath, the solution is filtered, and the undissolved matter is washed with dilute ammonia containing a little ammonium sulphide. From the filtrate the molybdenum trisulphide is recovered by adding dilute hydrochloric acid, and it is then converted in the usual way either into molybdenum disulphide or trioxide.

L. DE K.

Estimation of Tin in White Metals by Electrolysis. E. SCHÜRMANN (*Chem. Zeit.*, 1910, **34**, 1117—1118).—One gram of the alloy is covered with 10—15 c.c. of 50% solution of tartaric acid, and nitric acid, D 1·4, is then gradually added until the metal is dissolved. The solution is then diluted to 300 c.c., heated to boiling, and the tin precipitated by adding 10 c.c. of a 25% solution of sodium hydrogen phosphate in weak nitric acid. After diluting to about 600 c.c. with boiling water, the tin phosphate is allowed to settle, the liquid is siphoned off, and the precipitate washed by decantation with 900 c.c. of a 1% solution of potassium nitrate acidified with nitric acid. The washings are heated on the water-bath, when a further deposit is obtained, which is collected on a filter, and the main precipitate is then added. When drained, the precipitate is transferred to the beaker, in which the precipitation took place, and the little remaining in the filter is dissolved by means of 25 c.c. of hot *N*-potassium hydroxide. The alkaline liquid is then poured into the beaker, and, on warming, the tin phosphate soon dissolves. The solution is now neutralised with oxalic acid solution, and another 5 grams of the solid acid are added. Into the solution, occupying about 300 c.c., is passed, at boiling heat, a rapid current of hydrogen sulphide to remove any traces of antimony and copper. The filtrate is concentrated to 150 c.c., and neutralised with 80% aqueous potassium hydroxide; another 5 c.c. of the same are then added. The solution is then submitted to electrolysis, by preference in a Frary apparatus, using a current of 6—8 amperes and 4—5 volts; the operation is ended in two to two and a-half hours.

The process is also applicable to electrolytic tin. It does not give a clear solution with the tartaric-nitric acid mixture, but this makes no difference, as the separated stannic acid is dissolved afterwards by the potassium hydroxide. L. DE K.

Estimation of Gold by means of Hydrogen Peroxide. L. RÖSSLER (*Zeitsch. anal. Chem.*, 1910, **49**, 739—740).—Gold may be estimated by reduction with hydrogen peroxide in presence of sodium hydroxide. The author states that the addition of alkali is not strictly necessary, as the reduction also takes place in acid solution, but, owing to the fact that the operation takes a great many hours, the process is not of any practical value.

In presence of lithium or, preferably, potassium carbonate, the reduction is soon completed, and this fact may be utilised for gravimetric estimations of gold. L. DE K.

Detection of Ethyl Alcohol in Presence of Methyl Alcohol. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1910, [iv], **7**, 951—952. Compare this vol., ii, 357, 461).—The process depends on the fact that whilst bromine water has but little oxidising action on warm methyl alcohol, it converts ethyl alcohol on warming into acetaldehyde. The latter is detected by its power of restoring the colour to a solution of magenta decolorised by sodium hydrogen sulphite and hydrochloric acid. It is always advantageous to have a little methyl alcohol present, since this reacts with acetaldehyde to form dimethylacetal,

thus avoiding possible loss of the aldehyde. Details of the method of applying the test are given. T. A. H.

Estimation of Ethyl Ether and Benzene in Alcohol. HANS WOLFF (*Chem. Zeit.*, 1910, **34**, 1193).—The process is similar to the one recommended by Holde and Winterfeld (Abstr., 1908, ii, 435). One hundred c.c. of the spirit to be tested are diluted to D 0·96, and then submitted to distillation, the distillate being collected in a graduated cylinder. When 20 c.c. have passed over, 80 c.c. of brine are added, and the whole is thoroughly shaken. The volume of ether or benzene is then read off. The results are satisfactory, although a trifle too low, particularly in the case of ether. L. DE K.

Estimation of Phenol in the Urine of Oxen. CARL NEUBERG and A. HILDESHEIMER (*Biochem. Zeitsch.*, 1910, **28**, 525—528).—Mooser's statement (this vol., ii, 1039) that phosphoric acid may be used for the direct iodometric estimation of phenol and cresol in herbivorous urine is incorrect. The older modifications of the Kossler-Penny process must be employed both for diabetic urines and the urine of herbivora (on account of the glycuronic acid, pentoses, etc., in it). W. D. H.

Analysis of Cellulose Nitrates, Glycerol Nitrates, and Other Compounds from which Nitric Acid is Liberated by Concentrated Sulphuric Acid. EMILE BRONNERT (*Bull. Soc. ind. Mulhouse*, 1910, **80**, 254—259).—Stannous sulphate or stannous potassium sulphate is dissolved in 50 vol. % sulphuric acid, and a little hydrochloric acid is added to obtain a clear solution. This is then standardised as follows: 0·15 gram of pure potassium nitrate is dissolved in a few drops of water, and 50 c.c. of sulphuric acid and one drop of solution of diphenylamine are added. The tin solution is then run in from a burette until the bluish-violet colour has completely disappeared. The tin solution is then diluted with 50 vol. % sulphuric acid until it is of $N/10$-strength.

By means of this solution, commercial nitrates, spent acids, and also nitro-compounds, such as cellulose nitrates, which liberate nitric acid when dissolved in sulphuric acid, may be readily assayed. Attention is called to the uneven composition of some samples of commercial nitro-cellulose. L. DE K.

Estimation of Sugar by Reduction of Colouring Matters. NEUMANN WENDER (*Biochem. Zeitsch.*, 1910, **28**, 523—524).—A question of priority. The method described by Hasselbalch and Lindhard (this vol., ii, 905) as new, has been in use for many years (Crismer, 1888; Wender, 1890). W. D. H.

A Simple Method for the Estimation of Sugar in the Blood. II. The Sugar in the Blood. K. MOECKEL and E. FRANK (*Zeitsch. physiol. Chem.*, 1910, **69**, 85—88. Compare this vol., ii, 554).—By care in one or two points of detail, the method previously described can be utilised for the correct estimation of sugar in the blood, as well as in serum. W. D. H.

The Reducing Substances of Urine. CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1910, **69**, 72—75. Compare Abstr., 1909, ii, 902).—When known weights of dextrose are added to urine and the mixture titrated by Bertrand's method (Abstr., 1907, ii, 136), the amounts of dextrose found agree extremely well with the amounts added. When blood charcoal is used as a clarifying material before the estimation, the results are apt to come low. The addition of concentrated solutions of uric acid, creatinine, or urochrome to solutions of dextrose does not interfere with the estimation of the sugar; the reduction is the sum of the reductions of the dextrose and of the nitrogen compound. A loss is found, however, in working with dilute solutions, and this loss increases with the dilution. This is attributed to the diminution of the reduction of uric acid, urochrome, and especially of creatinine with an increase in dilution. This accounts for the fact that these substances possess no reducing properties in urine. The author suggests that the amount of creatinine present in normal urine is less than that usually accepted (0·6—2·1 grams per day), as normal urine shows no reducing action, whereas a solution containing this amount of creatinine is strongly reducing. J. J. S.

Reactions of Carbohydrates. I. Sucrose. C. REICHARD (*Pharm. Zentr.-h.*, 1910, **51**, 979—986).—A detailed description is given of the colour and other changes which take place when various reagents are allowed to react with solid sucrose.

Sulphuric, nitric, or hydrochloric acid, in the cold, converts sugar into a sticky mass, which does not dry on exposure to air. Sulphuric acid does not cause the separation of carbonaceous matter unless the preparation is heated. The green mixture of cupric sulphate and hydrochloric acid remains bright green much longer when sucrose is present. Sucrose inhibits to some extent the precipitation of mercurous chloride when hydrochloric acid is added to mercurous nitrate. A mixture of sodium arsenate with hydrochloric acid and sucrose gives a stable rose-red coloration. In presence of hydrochloric acid, sucrose gives a dark green coloration with potassium dichromate, blue with ammonium molybdate, and brown, changing to violet, with ammonium vanadate, but no coloration with sodium tungstate or with titanic acid in presence of sulphuric acid. A number of colour reactions with organic substances are also described, the most interesting of these are the red coloration given with tannic acid in presence of hydrochloric acid, and the gooseberry-red tint obtained with resorcinol and hydrochloric acid. The last two reactions and that with arsenic acid may be suitable for the detection of sucrose. T. A. H.

Detection of Dextrin by means of its Coloration by Iodine. GEORGES RIVAT (*Chem. Zeit.*, 1910, **34**, 1141).—Whilst a 1% iodine solution in water gives blue colorations of equal intensity with pure starch or with a mixture of starch and dextrin, a solution of 0·00012 gram of iodine in 1 c.c. of water gives a blue coloration at once with pure starch, but not with a mixture of starch and dextrin. In

the latter case the quantity of iodine that must be added before a blue tint is developed seems to vary with the amount of dextrin present. The observation may prove on further investigation to be the basis of a method of examining mixtures of starch with dextrins. T. A. H.

Modification of the Phenylhydrazine Reaction. JACOB BOESEKEN (*Chem. Weekblad*, 1910, **7**, 934).—As a substitute for phenylhydrazine, the author employs a solution of the base in sulphurous acid, which will dissolve up to 10%. This solution contains compounds of the formulæ $C_6H_5N_2H_3,SO_2$ and $(C_6H_5N_2H_3)_2,SO_2$, and is prepared by passing washed sulphur dioxide through a mixture of phenylhydrazine and the requisite quantity of water until solution is complete. At first a crystalline compound separates, but on further passage of the gas, it re-dissolves. Impurities are then filtered off. The reagent reacts at once with soluble aldehydes and ketones, and, on warming, with insoluble carbonyl compounds, the hydrazones being obtained in the pure state. Its efficacy has been tested with formaldehyde, acetaldehyde, acetone, benzaldehyde, *m*-nitrobenzaldehyde, acetophenone, cuminaldehyde, furfuraldehyde, *p*-chloroacetophenone, lævulic acid, acetylacetone, acetonylacetone, and ethyl acetoacetate.

When warmed with monoses at 80°, the reagent yields pure osazones. It has been tested with dextrose, lævulose, *d*-galactose, *d*-mannose, *l*-xylose, and rhamnose. A. J. W.

New Method for Estimating Volatile Fatty Acids. ERNST WELDE (*Biochem. Zeitsch.*, 1910, **28**, 504—522).—This is a method of steam distillation in a vacuum. The distillation lasts two hours; the temperature is 60°; proteins, fats, and carbohydrates remain unaltered, and bacterial action is inhibited. If acid is not added, the distillate contains the free volatile acids; if phosphoric acid is added, the total volatile acids are obtained. Illustrative experiments with milk, and contents of stomach and intestine are appended.

W. D. H.

Estimation of Formic Acid [in Formates]. ALFRED F. JOSEPH (*J. Soc. Chem. Ind.*, 1910, **29**, 1189—1190).—The process is based on the oxidation of formic acid by bromine water and the formation of free hydrobromic acid.

A few grams of the formate are dissolved to 200 c.c. of water, and, if necessary, made exactly neutral. Ten c c. of the liquid are heated to boiling, and bromine water is added until the colour no longer disappears. The excess of bromine is then expelled by boiling, and the liquid titrated as usual with standard alkali. In the case of sodium formate, 1 mol. of hydrogen bromide = 1 mol. of formic acid. A correction should be made for any acidity present in the bromine water employed.

In the presence of acetic acid, the titration process cannot be employed, but the formic acid may be calculated from the amount of total bromine left after boiling; this is best estimated by Volhard's thiocyanate method. In the case of sodium formate, 2 ats. of bromine = 1 mol. of formic acid. L. DE K.

Fission of Chloroform and Carbon Dioxide from Trichloroacetic Acid. ROBERT STOLLÉ (*Ber. Deut. pharm. Ges.*, 1910, 20, 371—372).—When trichloroacetic acid is heated in the presence of water and antipyrine, carbon dioxide and chloroform are evolved, and the latter substance may be detected by its odour. As a test for trichloroacetic acid, the author considers the use of antipyrine to be preferable to potassium hydroxide, as prescribed by the German Pharmacopœia, or to aniline (Abstr., 1906, i, 159); boiling with an excess of potassium hydroxide would not distinguish between trichloroacetic acid and chloral hydrate, whilst aniline has an odour which might mask that of the liberated chloroform. The author has prepared antipyrine trichloroacetate, m. p. 75°; it is a crystalline substance and is unstable. W. P. S.

A Reaction of Nopic Acid. OBDULIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1910, 8, 328—331).—To the solution of sodium nopate in a porcelain dish, 0·1 gram of resorcinol is added, and then 10—15 grams of concentrated sulphuric acid are poured gently on to the mixture. On gently warming for a few minutes, a violet coloration appears at the zone of contact of the two liquids, which changes first to intense blue and then to green, which persists. The above colour indication is given only by resorcinol, not by the isomeric dihydroxybenzenes, or by ordinary phenol, thymol, the naphthols, etc. The trihydroxybenzenes also fail to give a coloration, with the exception of phloroglucinol, which produces an intensely yellow coloration. The blue substance produced by sodium nopate in this test is insoluble in ether, is destroyed by water, and turns yellowish-red in presence of amyl alcohol. Some suggestions are given as to its possible nature. W. A. D.

Colorimetric Estimation of Hydrogen Cyanide. A. CHASTON CHAPMAN (*Analyst*, 1910, 35, 469—475).—The author shows that when a cyanide is treated with alkaline picrate solution, the product of the reaction may be either potassium *iso*purpurate or alkali salts of nitroamino-phenols; the *iso*purpurate is formed only when the cyanide is in excess, whilst an excess of picrate results in the formation of the nitroamino-phenols. In testing for cyanides, the picrate is usually in excess, and *iso*purpurate is not formed. The production of the nitroamino-phenols is the result of the reducing action of the cyanide, but other substances, such as acetone, aldehyde, hydrogen sulphide, etc., are also capable of reducing the picrate. If the reaction be employed for the colorimetric estimation of hydrogen cyanide, steps must be taken to prove that the coloration obtained is due to the presence of this substance alone. Small quantities of hydrogen cyanide may, however, be estimated by the process, provided that certain definite conditions precribed by the author be observed, but the test has, for the reasons mentioned, a very limited sphere of usefulness.

W. P. S.

Volumetric Estimation of Hydrogen Cyanide, Especially in and with Benzaldehydecyanohydrin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, 248, 529—533).—The process is a modification

of Andrews' method (Abstr., 1903, ii, 695). The indicator, iodoeosin and ether, is not affected by hydrogen cyanide, but is changed by the hydrochloric acid liberated in accordance with the equation :

$$HgCl_2 + 2HCN = Hg(CN)_2 + 2HCl.$$

The solution under examination, containing not more than 1% of hydrogen cyanide, is treated with $N/10$-sulphuric acid or potassium hydroxide in the presence of the indicator until the aqueous liquid is just rose-coloured. A solution of mercuric chloride (27·1 grams of mercuric chloride and 11·7 grams of sodium chloride in 500 grams of water), neutral to the indicator, is added, and the mixture is at once titrated, with shaking, with $N/10$-potassium hydroxide until the rose tint is restored in the aqueous liquid.

The total hydrogen cyanide in a solution containing benzaldehydecyanohydrin and free hydrogen cyanide is estimated as follows. The solution is first made neutral to the indicator. Then such an excess of $N/10$-potassium hydroxide is added that after shaking vigorously for a minute adding the mercuric chloride solution, and again shaking for a minute, the aqueous liquid is coloured strongly red; $N/10$-acid is added until the colour has disappeared, and the end-point is finally obtained by titrating back with $N/10$-alkali. The changes are shown by the equations: (i) $HCN + KOH = KCN + H_2O$; (ii) $KOH + CHPh(OH){\cdot}CN = KCN + Ph{\cdot}CHO + H_2O$; (iii) $2KCN + HgCl_2 = Hg(CN)_2 + 2KCl$.

The estimation of the free hydrogen cyanide in a solution containing hydrogen cyanide and benzaldehydecyanohydrin is performed as follows. Ten c.c. of the solution are run into a separating funnel containing about 20 c.c. of a neutralised, saturated solution of sodium sulphate (in which benzaldehydecyanohydrin is practically insoluble), 50 c.c. of ether and 10 drops of the 0·2% alcoholic iodoeosin are added, and the mixture is rendered neutral. After adding the mercuric chloride solution, the mixture is shaken thoroughly, and the aqueous layer is run into a vessel containing neutralised distilled water; the separating funnel is rinsed with a little sodium sulphate, and its contents are again shaken with 20 c.c. of the same solution. The aqueous liquid is run off, and, after again rinsing the funnel, the combined aqueous extracts, which contain an amount of hydrochloric acid equivalent to the free hydrogen cyanide in the original solution, are titrated with $N/10$-alkali as in the first case above. C. S.

Estimation of Citric Acid in Lemon Juice and Commercial Citrates. MATTEO SPICA (*Chem. Zeit.*, 1910, **34**, 1141—1142).—The method depends on the measurement of the volume of carbon monoxide produced when citric acid is heated with sulphuric acid, and a special apparatus for the purpose is described.

An Erlenmeye flask is closed by a hollow glass stopper forming part of the continu tion of an open cylindrical dropping funnel, provided with a three-way c k, and passing through this a glass tube prolonged into the flask, wher y a stream of carbon dioxide can be introduced and passed through t e flask. The terminal opening of the three-way cock is connected to a nitrometer. For each estimation, 2 grams of the citrate are placed in the flask, a little water added, and then carbon

dioxide is passed through until all air is expelled, as shown by complete absorption of the issuing gas in potassium hydroxide solution. Sulphuric acid (25 c.c.) is then run in from the dropping funnel, and carefully mixed with the citrate by shaking. The mixture is heated at from 80° to 100° and shaken continuously, the current of carbon dioxide being still maintained, and the issuing gas collected and measured with the usual precautions in the nitrometer filled with potassium hydroxide solution. One c.c. of carbon monoxide at 0°/760 mm. is equivalent to 0·009407 gram of citric acid. Carbonates may be estimated in commercial citrate by placing the weighed citrate in the flask, connecting up to a nitrometer filled with water, adding 25 c.c. of hydrochloric acid, and collecting and measuring the displaced air, which, after deducting 25 c.c. for the acid added, gives the volume of carbon dioxide formed. T. A. H.

Characterisation of Glycuronic Acid in Urine. R. BERNIER (*J. Pharm. Chim.*, 1910, [vii], **2**, 401—406).—Directions are given for the detection of glycuronic acid in urine by means of Tollens and Rorive's naphtharesorcinol reaction (Abstr., 1908, ii, 638; compare Mandel and Neuberg, *ibid.*, ii, 993), and by means of phenylhydrazine (Grimbert and Bernier, this vol., ii, 163, and Grimbert and Turpaud, *ibid.*, ii, 979).

Tollens and Rorive's reaction may be vitiated by the presence of indoxyl, and to avoid this difficulty the urine should first be defaecated with mercuric acetate. All the urines tested gave positive results with this reaction, thus affording a further proof that glycuronic acid is a normal constituent. T. A. H.

Detection of Benzoic Acid in Meats and Fats. KARL FISCHER and O. GRUENERT (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 580—583).—The following process for separating benzoic acid from a sample of meat or fat is described as being more useful and trustworthy than that described previously by the authors (Abstr., 1909, ii, 708); it is a modification of the process recommended by von der Heide and Jakob (this vol., ii, 359). Fifty grams of the material are heated with 150 c.c. of a 1% sodium hydrogen carbonate solution, the aqueous layer is then separated, neutralised with sulphuric acid, and treated with copper sulphate and sodium hydroxide. The mixture is then rendered slightly acid, filtered, the filtrate is acidified with sulphuric acid, and extracted with ether. The ethereal extract is now evaporated, and the residue obtained is tested for the presence of benzoic acid. For this purpose the test proposed by Jonescu (this vol., ii, 627) is the most trustworthy; it will detect the presence of 0·006% of benzoic acid in butter. Care must, however, be taken that only 1 mg. or so of the acid be employed in the test, and that a minimum quantity of hydrogen peroxide be used. The authors find that Robin's modification of Halphen's test is not suitable for identifying the benzoic acid extracted from fats, although it is capable of detecting very small quantities of pure benzoic acid. W. P. S.

Absorption Spectrum of Oils. RÉNE MARCILLE (*Ann. Falsif.*, 1910, **3**, 423—425).—The absorption spectrum of certain oils is due to

the presence of chlorophyll or its derivatives, the bands observed corresponding with the spectrum exhibited by this substance. Olive oil shows three bands, the principal one being at λ 665, whilst cotton-seed oil and sesamé oils show feeble absorption bands. Other oils, as a rule, do not exhibit absorption spectra unless they contain chlorophyll; this is sometimes the case with commercial linseed oil and castor oil. When the oils are heated with water, the position of the absorption bands is altered slightly. W. P. S.

Primary and Secondary Bromine Numbers of Oils. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1910, **23**, 2077—2078).—When a drying oil is dissolved in a suitable solvent and the solution treated with successive small quantities of bromine, the latter is absorbed until a point is reached where a trace of free bromine remains in the solution; the quantity of bromine thus absorbed constitutes the primary bromine number of the oil. A considerable excess of bromine must then be added in order that the oil may absorb a quantity of bromine corresponding with complete saturation of the oil. The following results were obtained with various oils: linseed oil, primary bromine number, 75·7; secondary number, 107·7; wood oil, primary number, 57·0; secondary number, 94·6; earthnut oil, primary number, 52·0; secondary number, 57·6. Non-drying oils do not give a primary bromine number. When calculated into iodine, the secondary or total bromine number of drying oils corresponds closely with the iodine number as estimated directly. The author discusses the relation of the primary and secondary bromine numbers to the composition of the oils. W. P. S.

Substitution of the Iodine Numbers of Fats by the Bromine Numbers. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1910, **23**, 2078—2080).—The author recommends that the bromine numbers of fats and oils be estimated in place of the usual iodine numbers, as the former number is more quickly obtained, and the results are trustworthy. The fat or oil should be dissolved in a somewhat large quantity of carbon tetrachloride, potassium bromide solution and water are then added, the mixture is acidified with hydrochloric acid, and, after the addition of a small crystal of potassium iodide, an excess of potassium bromate solution is introduced. The whole is well shaken in a stoppered flask for one minute, and the excess of bromine is titrated with sodium sulphite solution. The trace of iodine added as iodide serves as the indicator in the titration. W. P. S.

Analysis of Oils. RENÉ MARCILLE (*Ann. Falsif.*, 1910, **3**, 417—423).—The author recommends the Wys method for obtaining the iodine numbers of oils in preference to the Hübl method; the results yielded by the latter process vary according to the age of the reagent, the temperature at which the experiment is made, etc. Directions are given for preparing the Wys reagent and for estimating the iodine numbers of oils; the separation of the fluid fatty acids from an oil and the determination of the Tortelli number are also described. W. P. S.

Halphen's Reaction [for Cottonseed Oil]. LEOPOLD ROSENTHALER (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 453—454).—The amyl alcohol used in this test may be replaced by either methyl, ethyl, propyl, *iso*butyl, benzyl, or allyl alcohols, amylene hydrate (tertiary amyl alcohol), or santalol, but not by aldehydes, ethyl acetate, phytosterol, benzene, phenol, nitrobenzene, aniline, or acetic acid. When cottonseed oil is heated with a solution of sulphur in carbon disulphide, but without the addition of any alcohol, the characteristic coloration is not obtained; if the mixture is heated for a considerable length of time, a faint coloration may be obtained, but this is probably due to partial hydrolysis of the fat with the liberation of glycerol, which latter substance itself, when used in place of amyl alcohol, causes a coloration to be produced after thirty minutes' heating. A faint coloration also develops when ethylene glycol is employed. The solution of sulphur in carbon disulphide cannot be replaced by other sulphur compounds, such as allylthiocarbimide, potassium xanthate, disulphones, etc.

W. P. S.

The Kumawaga-Suto Method of Estimating Fats. YOSHITAKA SHIMIDZU (*Biochem. Zeitsch.*, 1910, **28**, 237—273).—The process of drying material which contains water leads to a loss of fat (10% or more), doubtless due to oxidation. The material should therefore be directly saponified by the Kumawaga-Suto method. Illustrative experiments with muscle, liver, blood, etc., are given. W. D. H.

Method for the Analysis of Fats by the Separation of the Solid Fatty Acids from the Liquid Acids. DAVID (*Compt. rend.*, 1910, **151**, 756—757).—The method is based on the observation that the ammonium salts of the solid fatty acids are quite insoluble in large excess of aqueous ammonia at 14—15°, whilst the ammonium salts of the liquid acids are soluble.

A mixture of solid and liquid acids can be separated by dissolving 2 grams in 5 c.c. of warm 95% alcohol; 50 c.c. of pure ammonia are added, and the solution warmed until bubbles of gas begin to be evolved. After remaining several hours at a temperature not exceeding 15°, the liquid is filtered, the ammonium stearate or palmitate washed with ammonia until the filtrate gives no turbidity with barium hydroxide, and then treated on the filter with hydrochloric acid diluted with its own volume of water at 22°. The fatty acids are washed with hydrochloric acid, and finally with water, dried at 100°, and weighed. The experimental error does not exceed 0·2—0·3%.

The process is applicable to mixtures containing other solid acids, such as hydroxystearic, *iso*oleic, lauric, and arachidic acids, and is believed to be of general application. W. O. W.

The Electrical Conductivity of Milk, and the Use of this Constant for the Detection of Watering and Addition of Electrolytes. RINALDO BINAGHI (*Biochem. Zeitsch.*, 1910, **29**, 60—78).—The electrical conductivity of fresh unadulterated milk is approximately a constant for each species. For milk of sheep, K_{25}(mean) $= 50{\cdot}40 \times 10^{-4}$; for that of goat, $49{\cdot}00 \times 10^{-4}$; for cow's milk, $48{\cdot}70 \times 10^{-4}$. The

conductivity diminishes in proportion to the water added. Electrolytes which are added for preservative purposes (borates, etc.) increase the conductivity. The measurement of this constant is recommended for detecting adulteration and addition of preservatives. S. B. S.

The Tests for Purity of Quinine Salts. FRANK TUTIN (*Pharm. Journ.*, 1909, [iv], 29, 600—603).—The methods adopted by the various national pharmacopœias for the detection of impurities in quinine salts are of two kinds: (1) the ammonia test, and (2) specific tests for certain impurities. The author has investigated the effects of various conditions on the results obtained by the application of these two kinds of tests, more particularly as regards the former, and finds that the best method of carrying out the ammonia test is that prescribed in the French Codex, which, however, is only applicable to quinine sulphate. The ammonia test being of limited applicability, the test for cinchonine and cinchonidine prescribed by the British Pharmacopœia is preferable, since it can be used for any quinine salt. The following general conclusions are drawn.

The minimum amount of 10% ammonia solution which will yield a clear solution at 15° with 5 c.c. of a solution of quinine sulphate saturated at 15° is 4·4 c.c., so that it is impossible to meet the requirements of the German Pharmacopœia, which stipulates 4 c.c. of ammonia solution. A reasonable requirement for commercial quinine sulphate would be 6·0 c.c. The quantity of ammonia needed is affected by the alkalinity or acidity of the quinine sulphate used, so that it is not a trustworthy indication of the presence of other alkaloids. In this connexion it is pointed out that solutions of commercial quinine sulphate in water are usually slightly alkaline, and become more so on heating, reverting to their original slight alkalinity on cooling. In applying the ammonia test to quinine salts other than the sulphate, it is usual to convert them into the sulphate in such a way that the test is made in presence of an inorganic salt. The presence of the latter profoundly influences the quantity of ammonia needed, so that the test becomes untrustworthy. For this reason the specific test for cinchonine and cinchonidine prescribed by the British Pharmacopœia is more satisfactory, but in applying it "Aether purificatus," not "Aether," of the Pharmacopœia should be used. The ammonia test is, however, the only one available for the detection of hydroquinine, but it is not yet certain that minute quantities of hydroquinine sulphate are objectionable in quinine sulphate. The specific rotations quoted in the French Codex for several quinine salts are not in harmony with each other, and could not be confirmed.

The following new salts were prepared: *Quinine* d-*camphorsulphonate,* m. p. 191°, colourless needles from water or dilute alcohol. *Quinine* d-*bromocamphorsulphonate,* m. p. 260° (decomp.), crystallises from dilute alcohol, but is insoluble in water. *Hydroquinine* d-*camphorsulphonate,* m. p. 217—218°, and d-*bromocamphorsulphonate,* m. p. 266°, are both crystalline. T. A. H.